THERE IS VERY LITTLE MARGIN BETWEEN THE LEFT AND RIGHT PAGES

SILICONES

and other

ORGANIC SILICON COMPOUNDS

by

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Preface

With the advance of chemical science, there came into being the necessity for specialization. It became impossible for any one worker to concentrate on the entire subject of chemistry. Thus there arose those who called themselves Inorganic Chemists or Organic Chemists. But as this specialization resulted in the setting up of more and more restricted fields, the border areas were neglected. Thus the chemistry of organic silicon came into being. It is neither organic nor inorganic, yet it is both.

Some of the properties of these compounds are additive, partaking of the nature of both the organic and inorganic parent, while some are distinctive. It is to these properties that we owe the tremendous, and still mounting, interest that modern chemists the world over are showing in the organic chemistry of silicon.

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Contents

Chapter 1

Introduction

Organic chemistry abounds in substitution reactions, both direct and indirect: halogen for hydrocarbon hydrogen, primary amino for halogen, hydroxyl for primary amino, etc. But the most important of these in its effects on the compounds themselves would be replacement of the carbon atom by some other element, for instance from column four of the Periodic Table. As a matter of fact, replacement of carbon was predicted at a very early date by none other than Dumas himself[414].

As evidence that this concept of substitution was not without effect on the scientific thinking of later years, the following quotation from *Chemical Abstracts* may be cited, referring to an address delivered by J. E. Reynolds in 1909 which was published more or less in full[163]: "A discourse delivered before the Royal Institution. It contains no new matter. The author advances a speculative theory as to the probability of a 'high-temperature protoplasm' containing silicon in place of carbon and phosphorus instead of nitrogen and points out that silicon found in certain animal and plant cells may actually be a constituent of the protoplasm of such cells."

Within the body of chemical literature of the nineteenth and twentieth centuries will be found contributions describing this more fundamental type of substitution, which has been hinted at in the references already given—namely, the indirect substitution of another fourth column element for carbon. Of these substitutions by far the most important is silicon for carbon.

The term "organic compounds of silicon" will be taken to mean those compounds of silicon which contain carbon of such a character as definitely to impart organic properties to the molecule. Thus there will be found included here such compounds of silicon as are analogous to hydrocarbons, halides, alcohols, aldehydes, ketones and ethers; but under this definition silicon carbide, tetrachlorosilane and trichlorosilane as such will be excluded. Because of their value in synthetic work, however, some of these compounds outside the classification of organic compounds of silicon will be given a certain amount of consideration.

After laying a foundation with halides, the discussion will proceed to

cover more theoretical and synthetic work on organic compounds of silicon carried out for the most part before 1935. To Frederick S. Kipping we are indebted for a tremendous volume of careful groundwork in this field, and to Kipping we who are still interested in the organic chemistry of silicon revert for data, methods and general information. Because these papers, discussed in Chapter 3, are of slightly older vintage than some others and have come from solely academic sources, they will be treated as a unit.

Later syntheses of organic compounds of silicon are grouped in two classes depending on the type of reaction by which they are carried out. An entire galaxy of methods and processes is brought about at moderate heat by the use of metallorganic compounds such as the Grignards, lithium compounds, etc.; another group, perhaps not so distantly related in mechanism, makes use of higher temperatures, organic halides in the vapor phase and silicon metal activated, for example, by finely divided copper.

To complete the survey, compounds will be discussed which border on the types known as orthoesters, acetals, ketals and others, *i.e.*, those containing silicon connected to carbon through oxygen or sulfur. Here the field has already been covered to a certain point[84] and this book will therefore aim only to bring the subject up to its own date of publication.

In this connection there is a comment by Friederick Wöhler[348] which should not be overlooked: "I believe that one of these formulae must express the true structure of the molecule but in any case it is of paramount interest in that it can be regarded as a kind of compound, constructed under the rules of organic chemistry, in which silicon plays the role of carbon. Perhaps it initiates a type of an entire series of similar compounds, and it may give rise then just as is now known to be true of carbon, to an entirely new branch of chemistry, that of silicon." To which Friedel and Ladenburg[63] after quoting, laconically added: *"Mann kann nicht klarer sein!"*

The writer is indebted to Mr. Matthew Hayes of the Houdaille-Hershey Co., Buffalo, N. Y., for a contribution summarizing two papers with whose contents Mr. Hayes is thoroughly familiar[336, 337].

The permission of H. M. Stationery Office, through its Controller, has been obtained for the verbatim reproduction of portions of British patents contained herein and copies of these patents have been purchased from the Controller of Patents.

With this brief description of purpose this volume is presented for the information of workers in the field who never tire of pushing back the frontiers of knowledge.
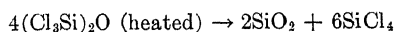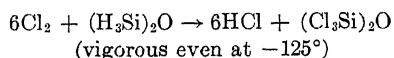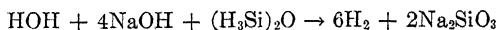
Chapter 2

Halogenated Silanes

Syntheses of silico organic compounds, listed in succeeding chapters, require as their intermediates certain inorganic compounds of silicon—generally some halogen derivative, with or without oxygen. For this reason this chapter, roughly outlining certain methods of preparing halogenated silanes, has been included before going on to the strictly organic compounds which are the primary interest of this book. The preparation of these halogenated silanes and some of their allied oxygen derivatives is not new.

Silane has been prepared by the action of hydrochloric acid on magnesium silicide[184, 185]; in the latter reference mention will be found of a by-product, the silicon analog of oxalic acid. In 1916, Stock and Somieski[151] published methods for preparing the series of compounds, silane and its three higher homologs. Magnesium silicide was treated with hydrochloric acid and from the mixture of products these were separated. For purposes of comparison the physical properties are listed in Table 1.

Table 1. Silane and its Homologs.

	b.p. (°C)	m.p. (°C)	d
SiH_4	-112	-185	0.68 $(-185°)$
Si_2H_6	-15	-132.5	0.686 $(-25°)$
Si_3H_8	?	-117	0.725 $(0°)$
Si_4H_{10}	?	-93.5	0.79 $(0°)$

Stock, Somieski and Wintgen[145] determined the physical properties of disiloxane; they discovered that it reacts with water, even though insoluble, forming hydrogen gas and a polymerizable silicon analog of formaldehyde. Reactions with sodium hydroxide of 30 per cent strength and with chlorine were also investigated:

$$HOH + 4NaOH + (H_3Si)_2O \rightarrow 6H_2 + 2Na_2SiO_3$$

$$6Cl_2 + (H_3Si)_2O \rightarrow 6HCl + (Cl_3Si)_2O$$
$$\text{(vigorous even at } -125°)$$

$$4(Cl_3Si)_2O \text{ (heated)} \rightarrow 2SiO_2 + 6SiCl_4$$

3

The same authors[147] studied the hydrolysis of dibromooxosilane and the analysis of the product with sodium hydroxide, by hydrogen evolution:

$$SiOBr_2 + HOH \rightarrow HBr + (H_2SiO)_x \text{ (not isolated)}$$

$$(H_2SiO)_x + NaOH \rightarrow H_2 + Na_2SiO_3$$
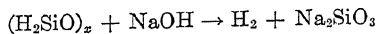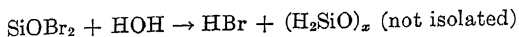
And again, Stock and Somieski[117] in 1918 reported that the decomposition of silane in water catalyzed by alkali is definitely catalyzed also by the alkali in the glass beaker or other container. Slightly acidified water retarded this decomposition and consequent evolution of hydrogen, but more strongly acidified media again proved to be positive catalysts. As the reaction was slow, the method was satisfactory for analysis of a mixture of silane, hydrobromic acid and bromosilane, as explained in the original paper; for instance, hydrobromic acid was dissolved during the course of the reaction, and the other two compounds reacted as:

$$2H_3SiBr + HOH \rightarrow 2HBr + H_3Si)_2O \quad \text{(fast)}$$

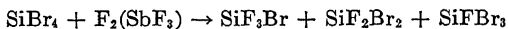$$(H_3Si)_2O + 3HOH \rightarrow 6H_2 + 2SiO_2 \quad \text{(slow)}$$
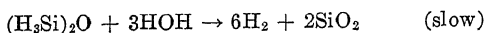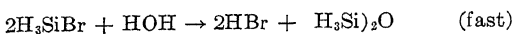
Analysis proceeded by measuring the successive volume changes. Bromination of silane will be discussed under bromine derivatives (p. 000).

Ruff and Albert[240, 241] studied the interchange of halogens between trichlorosilane and various inorganic fluorides. There seemed to be two patterns for this reaction. In some cases, using antimony or arsenic, tetrafluorosilane was formed, and when tin or titanium was used the product was trifluorosilane.

Schwartz and Liede[198] presented data on the preparation and hydrolysis of tetrafluorosilane in 1920. This contribution was later followed by a paper from Father Nieuwland's laboratory[172] describing the use of the compound as an esterification catalyst in the field of carbon chemistry.

Schumb and Anderson[173] prepared mixed fluorobromosilanes by two methods:

$$Si_2F_6 + Br_2 \rightarrow SiF_3Br + SiF_2Br_2 + SiF_4$$

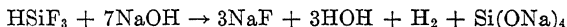$$SiBr_4 + F_2(SbF_3) \rightarrow SiF_3Br + SiF_2Br_2 + SiFBr_3$$

A German patent[180] dated 1929 covers the formation of tetrafluorosilane by the interaction of silicic acid, a fluoride and chlorine, or some substance that would produce free chlorine. High temperatures must be used here, and a reducing agent, either solid or gaseous, must also be present. For the latter, to quote the patent, carbon monoxide or dioxide can be used.

Booth and Swinehart[174, 175] have prepared several mixed fluorochlorosilanes. The first reference, dated 1932, covered the interaction of tetrachlorosilane and antimony trifluoride in the presence of antimony

pentachloride, chlorine, or some other catalyst of similar nature. The products were fluorotrichlorosilane, difluorodichlorosilane and trifluorochlorosilane. These three compounds and tetrafluorosilane were again prepared three years later[175] by the direct fluorination of tetrachlorosilane in the presence of antimony trifluoride and trichloride.

In 1934, Booth and Stilwell[233] fluorinated trichlorosilane by the action of antimony trifluoride in the presence of the pentachloride as before. The products were HSiFCl₂ in quite good yields with lesser amounts of HSiF₂Cl. Trifluorosilane proved to be unstable even at the temperatures obtained by the use of liquid nitrogen. Treatment with caustic produced hydrogen gas, probably in accordance with the following equations:

$$HSiFCl_2 + 7NaOH \rightarrow NaF + 2NaCl + 3HOH + H_2 + Si(ONa)_4$$

$$HSiF_3 + 7NaOH \rightarrow 3NaF + 3HOH + H_2 + Si(ONa)_4$$

Difluorosilane has been prepared[217] by the action of antimony trifluoride on chlorosilane and dichlorosilane.

I. G. Farbenindustrie[213] in 1937 patented in France a method for the preparation of tetrafluorosilane by the interaction of calcium fluoride, silica and sulfuric acid.

More attention has been given to chlorosilanes than to the fluoro compounds. Buff and Wöhler[234, 235] passed hydrohalogen acid vapors over heated crystalline silicon. The formulas of the products were given as "Si₂Cl₃ + 2HCl," "Si₂Br₃ + 2HBr," and "Si₂I₃ + 2HI." However, recalculation of their data on the basis of more modern atomic weights would seem to indicate that the correct formulas are HSiCl₃, HSiBr₃ and HSiI₃.
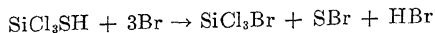
Friedel and Ladenburg[62] hydrolyzed trichlorosilane with ice water. The product was a white powder not unlike silica in appearance. There must have been some hydrogen which remained attached to the silicon in this product, since standard treatment with caustic resulted in the usual evolution of hydrogen gas. Based on the amount of hydrogen thus liberated, Friedel and Ladenburg concluded that there were two hydrogens per molecule of product:

$$2HSiCl_3 + 3HOH \rightarrow 6HCl + \underset{\underset{O}{\|}}{H-Si}-O-\underset{\underset{O}{\|}}{Si-H}$$
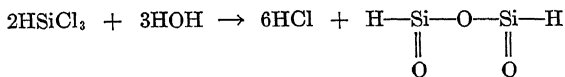
The torch seems indeed to have passed to Friedel and Ladenburg[63] with emphasis on the simpler chemistry of the halogen derivatives of silicon, the halogenated silanes. Their next contribution dealt with the action of hydrogen sulfide on tetrachlorosilane:

$$SiCl_4 + HSH \rightarrow Cl_3SiSH + HCl$$

$$Cl_3SiSH + 4C_2H_5OH \rightarrow HSH + 3HCl + Si(OC_2H_5)_4$$
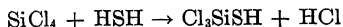
A third equation is reproduced here without comment:

$$SiCl_3SH + 3Br \rightarrow SiCl_3Br + SBr + HBr$$

In 1868, Friedel and Ladenburg[64] passed vapors of tetrachlorosilane through a heated tube of porcelain packed with feldspar, obtaining various oxychlorides of silicon. Troost and Hautefeuille[135, 136, 138, 140, 164, 342] added considerably to the known technique of preparing halogenated silanes and mixed oxygen-chlorine products. In general, their methods embraced the passage of mixed oxygen and chlorine vapors over heated silicon, but analytical data seem to be meager.

Warren[256, 339] has described the preparation of tetrachlorosilane by the action of chlorine on heated ferrosilicon of 15 per cent silicon content. It was mentioned here that bromine as well as iodine replaced chlorine in tetrachlorosilane giving the corresponding tetrasubstitution product.
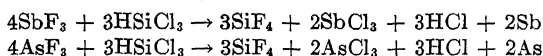
In 1889, Ludwig Gatterman[165] prepared metallic silicon and a magnesium silicide by the action of metallic magnesium on silicon dioxide.:
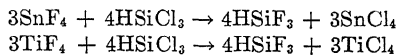
$$SiO_2 + 4Mg \rightarrow Mg_2Si + 2MgO$$
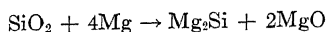
Actually, it seemed best to use an inverted molar ratio, namely four of sand to one of magnesium, because the reaction took place almost entirely on the surface of the former. Magnesium silicide reacted with hydrochloric acid to give silane and magnesium chloride. $SiCl_4$, $SiBr_4$ and SiI_4 were made by direct contact at high temperatures, the last being slowest in synthesis and requiring the most heat. Iodine vapor was carried through the system by carbon dioxide. Silicon and dry hydrogen chloride yielded trichlorosilane, which was capable of hydrolysis to $H_2Si_2O_3$, perhaps 1,3-dioxodisiloxane. This product reacted further with dilute ammonium hydroxide over platinum, yielding hydrogen and silica. Tribromosilane was prepared from hydrobromic acid and silicon. In collaboration with Weinlig, Gatterman[166] continued the work, preparing hexachlorodisilane and octachlorotrisilane[73, 166] as by-products of the synthesis of tetrachlorosilane.

In 1892 a note appeared[239] to the effect that Combes had prepared the anhydride of silicoformic acid and had found it quite resistant to the action of nitric acid, of aqua regia and of bromine at 180°. Four years later, Combes[238] presented a synthesis of trichlorosilane by the action of hydrogen chloride on silicon.

Ruff and Albert[240, 241] investigated halogen interchange between trichlorosilane and certain inorganic fluorides. These reactions were capable of division into two classes, as mentioned earlier in this chapter:

$$4SbF_3 + 3HSiCl_3 \rightarrow 3SiF_4 + 2SbCl_3 + 3HCl + 2Sb$$
$$4AsF_3 + 3HSiCl_3 \rightarrow 3SiF_4 + 2AsCl_3 + 3HCl + 2As$$

$$3SnF_4 + 4HSiCl_3 \rightarrow 4HSiF_3 + 3SnCl_4$$
$$3TiF_4 + 4HSiCl_3 \rightarrow 4HSiF_3 + 3TiCl_4$$

Besson and Fournier[167, 168, 169] prepared chlorosilane and dichlorosilane by the low-temperature action of hydrochloric acid on silicon. The reducing action of calcium hydride on tetrachlorosilane formed a small amount of trichlorosilane. Passing an electric spark through a mixture of hydrogen and trichlorosilane formed tetrachlorosilane, hexachlorodisilane, octachlorotrisilane, dodecachloropentasilane, and quadradecachlorohexasilane. Trichlorosilane reacted with oxidizing agents such as oxygen, ozone, and nitric oxide to form various oxoderivatives, for instance hexachlorodisiloxane.

Besson and Fournier[182] confirmed their own predictions[183] that a mixture of hydrogen and bromochlorosilane, when sparked, would produce complex higher homologs of the halogen derivatives used. They were also successful in working up this method as a means of preparing oxygen-free products of this type using, *e.g.*, hydrogen, bromine and tetrachlorosilane. Hexachlorodisilane and octachlorotrisilane were also formed, but could not be removed by fractionation. There was also a certain amount of disproportionation:

$$2SiCl_2Br_2 \rightarrow SiCl_3Br + SiClBr_3$$

Iodine was found to behave somewhat like bromine. Separation of these compounds was incomplete.

Burning of silicon in an atmosphere of mixed oxygen and chlorine[186] formed various oxychlorides which, when treated with sodium salts of organic acids, formed the anhydrides of these acids. Thus with sodium acetate the yield of acetic anhydride amounted to 82 per cent; with sodium propionate the yield of propionic anhydride was 60 per cent. Sanger and Riegel[187] found that sulfur trioxide reacted with tetrachlorosilane forming a mixture of oxychlorides of sulfur and silicon.

Hexachlorodisilane has also been prepared by Geoffrey Martin[79] from ferrosilicon. The original paper is unusually complete with respect to experimental details.

Stock, Somieski and Wintgen[145] chlorinated disiloxane obtaining hexachlorodisiloxane. The reaction was vigorous even at $-125°$.

Hutchins[242] has presented data on the preparation of tetrachlorosilane, and Richter[243] discussed chlorides of silicon and titanium as smoke clouds during World War I.

Two patents[190, 191] dated 1918 covered the preparation of tetrachlorosilane by the action of dry chlorine on silicon carbide above 1000°. External heating was not necessary once the reaction got under way.

In 1919, Stock and Somieski[98] prepared chlorosilane by the action of hydrochloric acid on silane in the presence of aluminum chloride. Di-

chlorosilane was also formed to the extent of 20 per cent of the total yield. The same authors reported a study[194] of the silicon analog of formaldehyde and some of its polymers. The hydrolysis of gaseous dichlorosilane was simple, giving a gaseous monomer:

$$H_2SiCl_2 + HOH \rightarrow 2HCl + H_2SiO$$
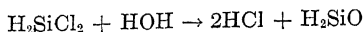
This monomer polymerized slowly in the gaseous phase; but on cooling with liquid air it went over to liquid and solid polymers, each of which reacted with sodium hydroxide:

$$(H_2SiO)_x + 2xNaOH \rightarrow 2xH_2 + xNa_2SiO_3$$
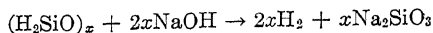
Some of these polymers were soluble in benzene and their molecular weights, determined cryoscopically, showed that the value of x was never less than 6. These benzene solutions could most easily be prepared by hydrolyzing a benzene solution of dichlorosilane. The polymers were stable toward water, reduced silver nitrate in the cold but did not reduce copper sulfate. Monomeric oxosilane had a much greater tendency to polymerize than formaldehyde. Stock continued the discussion of polymerized oxosilanes in still another paper[197].

Moore[196] patented the synthesis of tetrachlorosilane by the action of chlorine on silicon or silicon carbide.

In 1920, Stock and Somieski[199] reported that the action of hydrochloric acid on disilane in equal proportions by volume, or proportions calling for more than one volume of acid to one of disilane, formed dichlorodisilane and trichlorodisilane when the reactions were catalyzed by aluminum chloride. The polychlorodisilanes showed structural isomerism, just as do the corresponding carbon compounds. A large excess of hydrochloric acid did not lead to the formation of hexachlorodisilane. Hydrobromic acid reacted more readily than did hydrochloric acid, giving bromodisilane and dibromodisilane. These halogenated disilanes were observed to hydrolyze to disiloxanes, in the form of white solids. The chloride seemed to be more resistant than was expected to the action of sodium hydroxide. A second paper along these lines[200] discussed the action of ammonia on chlorosilane and dichlorosilane.

A British patent dated 1922[201] covers the preparation of tetrachlorosilane by the action of chlorine gas containing a certain amount of disulfur dichloride on "an oxide and carbon." This method, or a similar one, appeared again in 1926[205].

Stock and Zeidler[244] prepared trichlorosilane, as did Combes,[238, 239] and then carried out experiments in hydrolyzing it. Their results checked with those of others with respect to the formation of the anhydride of silicoformic acid, or 1,3-dioxodisiloxane. Stock and Somieski[245] in the same

year reported further investigations on the chemistry of disilane and dichlorosilane.

Quig produced tetrachlorosilane by the action of chlorine on ferrosilicon[178].

The preparation of fluorochlorosilanes has already been discussed[174, 175].

The action of hydrochloric acid on silane to form chlorosilane is slow[117].

Reinbold and Wisfeld[141] more recently (1935) have repeated and confirmed the preparation of hexachlorodisiloxane and octachlorotrisiloxane previously prepared by others.

Schumb and Anderson[207] fluorinated the three possible chlorobromosilanes and have prepared fluorochlorodibromosilane and fluorodichlorobromosilane. These compounds have also been formed by the action of chlorine or of antimony trichloride on fluorotribromosilane. The chlorination of tetrabromosilane by means of antimony trichloride or phosphorus trichloride formed all three possible chlorobromosilanes, as did also direct chlorination with chlorine and bromination of hexachlorodisilane with free bromine. The two compounds mentioned above, containing fluorine, chlorine and bromine, all hydrolyzed in moist air.

High homologs of chlorinated silane were formed by Schwarz and Meckbach[208] by the action of hydrogen, free of oxygen, on tetrachlorosilane over quartz rods, at temperatures between 1000° and 1100°. The products were condensed by liquid air. Schwarz and Pietsch[209] in 1937 reported formation of pentachlorodisilane and of dichlorosilicon by a similar reaction, passing the vapors of hydrogen and tetrachlorosilane between aluminum electrodes with 10,000 volts between them. The products were cooled by liquid air.

A Japanese patent[231] dated 1933 described the passing of chlorine gas into a mixture of crushed rocks, clay and carbon. The products included chlorides of aluminum, silicon and iron, which were separated by fractional distillation.

Trichlorosilane was prepared by Booth and Stilwell[232] by passing hydrogen chloride over various copper-silicon alloys. These alloys were determined to be Cu_2Si, $CuSi$, and $CuSi_2$, prepared by pressing the mixed powdered metals at 60,000 psi and sintering the resulting pellets in an atmosphere of hydrogen at 900°. Hydrogen chloride was generated by dropping hydrochloric acid on concentrated sulfuric acid; the complicated sealed glass set-up was described in quite satisfactory detail in the original article. Booth and Stilwell commented that there seemed no objection to the use of glass stopcocks provided that the gases were kept moving through the system at a pressure lower than the vapor pressure of trichlorosilane at room temperature. A temperature of 380° was found optimum.

Maddock, Reid and Emeleus[217] caused chlorosilane and dichlorosilane to react with antimony trifluoride, by which reaction difluorosilane was formed. Schwarz and Gregor[218] in 1939 claimed the preparation of SiCl.

Detailed practical procedures for the preparation of halogenated silanes were given by Schumb and Gamble[170] under date of 1939.
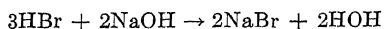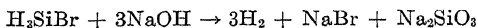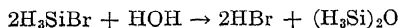
Andrianov[222] has prepared tetrachlorosilane by the action of chlorine on ferrosilicon at 550° with a yield of 90 per cent.

The passage of hydrobromic acid vapors over heated crystalline silicon[234, 235] was found by Buff and Wöhler to give a compound which they described as "$Si_2Br_3 + 2HBr$." In 1889 Ludwig Gatterman[165] treated silicon with bromine, obtaining tetrabromosilane.

Besson and Fournier[183] found that hydrobromic acid on amorphous silicon metal generated tetrabromosilane, with small amounts of tribromo-, dibromo- and bromosilane as by-products. The vapor of tribromosilane, when subjected to an electric spark, produced tetrabromosilane and hexabromodisilane, both existing as isolable white crystals. Decabromotetrasilane was also found as a product of this decomposition and resynthesis. The work of Besson and Fournier on chlorobromosilanes has already been discussed[182].

In 1917, Stock and Somieski[144] prepared two brominated silanes and studied their hydrolysis. The bromination of silane is ordinarily rather violent; but here, using an excess of silane with solid bromine on the walls of the flask and keeping the temperature between $-70°$ and $-80°$, a reasonably pure yield of bromosilane and of dibromosilane was obtained. Even with all these precautions, the reaction was not at all easy to carry out.

Bromosilane is a colorless gas with a pungent odor; it detonates on contact with air. Hydrolysis with caustic yields hydrogen quantitatively:

$$2H_3SiBr + HOH \rightarrow 2HBr + (H_3Si)_2O$$

$$H_3SiBr + 3NaOH \rightarrow 3H_2 + NaBr + Na_2SiO_3$$

$$3HBr + 2NaOH \rightarrow 2NaBr + 2HOH$$

Dibromosilane is a colorless liquid, quite mobile, burning in air and very sensitive to moisture, giving HBr and a solid which is probably $(H_2SiO)_x$. It also generates hydrogen with caustic alkali:

$$H_2SiBr_2 + 4NaOH \rightarrow 2H_2 + 2NaBr + HOH + Na_2SiO_3$$
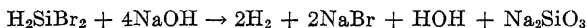
The hydrolysis of dibromooxosilane[147] and the work of Stock and Somieski[117] on the preparation of disiloxanes from bromosilane have already been discussed. Bromination of silane for three hours by means of hydrobromic acid and aluminum bromide gave 25 per cent of H_3SiBr, 33 per cent of H_2SiBr_2, and 42 per cent of unchanged SiH_4. The reaction with hydriodic acid was found to be slower.

Schumb and Young[179] investigated the reaction between hydrobromic acid and crystalline silicon and have reported that it was not noticeable below 340°, but at 360° it proceeded readily. As the temperature was raised the formation of tetrabromosilane increased, while that of tribromosilane decreased. At 700° the following reaction took place:

$$HSiBr_3 \rightarrow SiBr_4 + Si + H_2$$

It was believed that the primary products were tetrabromosilane and hydrogen, which interacted after formation to produce tribromo- and dibromosilane. Schumb and Klein[142] in 1937 showed the existence of a homologous series, with the exception of the tetramer $(SiOBr)_4$, having the general formula $Si_nO_{n-1}Br_{2n+2}$, of which $SiBr_4$ was the first. This series is now known as far as $Si_6O_5Br_{14}$.

The preparation of mixed fluorobromosilanes has already been mentioned[173].

Schumb[228] presented a method of preparing dibromosilane, tribromosilane and tetrabromosilane by the action of gaseous hydrobromic acid on 40-mesh silicon.

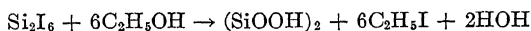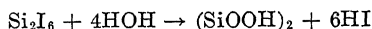The earliest recorded work on iodosilanes[234, 235] described the formation of "$Si_2I_3 + 2HI$" by the action of HI on crystalline silicon. Later, in 1880, Friedel and Ladenburg[69, 559] presented a rather remarkable paper describing the results of their investigations into the chemistry of certain iodosilanes, including the still mysterious reactions by which hydrogen is evolved. Hexaiododisilane was prepared by the action of metallic silver on tetraiodosilane at 290°–300° and the product was subjected to hydrolysis:

$$2SiI_4 + 2Ag \rightarrow 2AgI + Si_2I_6$$

$$Si_2I_6 + 4HOH \rightarrow 2SiO_2 + 6HI + H_2$$
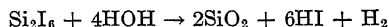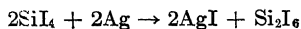
Distillation of hexaiododisilane, however, gave a residue insoluble in CS_2, $CHCl_3$, C_6H_6 and $SiCl_4$. Judging by its hydrolytic reactions it was SiI_2:

$$SiI_2 + 2HOH \rightarrow SiO_2 + 2HI + H_2$$

but it could have been a polymer of some sort. With ice water the disilane gave no hydrogen but rather a compound which was probably the silicon analog of oxalic acid:

$$Si_2I_6 + 4HOH \rightarrow (SiOOH)_2 + 6HI$$

$$Si_2I_6 + 6C_2H_5OH \rightarrow (SiOOH)_2 + 6C_2H_5I + 2HOH$$

$$(SiOOH)_2 + 4KOH \rightarrow 2Si(OK)_2 + 2HOH + H_2$$

Free bromine acting on hexaiododisilane produced hexabromodisilane and mercuric chloride replaced all the iodine with chlorine.

Tetraiodosilane was later prepared[165] by direct addition at high temperatures. The reaction was slow, however, and required more heat than the addition of chlorine or bromine. Iodine vapor was carried through the system by a stream of carbon dioxide. Besson and Fournier[182] have prepared chloroiodosilanes.

Maddock, Reid and Emeleus[217] were successful in bringing about the interaction of silane and hydriodic acid. Apparently the introduction of one iodine in place of one hydrogen:

$$SiH_4 + HI \rightarrow H_2 + H_3SiI$$
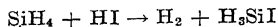
must have increased the reactivity of the remaining hydrogens, because all possible iodine replacement products were found—that is H_2SiI_2, $HSiI_3$ and SiI_4—in addition to the one listed above. Both iodosilane and and diiodosilane turned brown readily in air and both reacted with mercury. Magnesium reacted with iodosilane to form a product of the Grignard type. In the original reaction between hydriodic acid and silane, a temperature of 80° was found to give optimum yields with aluminum iodide as the catalyst. The same authors in 1941[227] repeated the work even more carefully, isolating H_3SiI and H_2SiI_2 and determining their physical constants and properties. Neither of these products was found to be spontaneously inflammable in air, but the vapor of each burned.

In 1942, Schwarz and Pflugmacher[229] treated tetraiodosilane with silver for six hours out of contact with air, at 280°. The product was hexaiododisilane. This product decomposed to a slight extent on distillation giving a certain amount of tetraiodosilane once more. The residue remaining after this distillation was treated with water to form $(H_2Si_2O_3)_x$, which was assumed to be a linear polymer.

# Chapter 3

The Work of Frederick S. Kipping and Others

Many chemical investigations owe their inception to the interest of the manufacturer; on the other hand, many are started as a result of the persistence of some investigator in academic surroundings. To both these sources of information the organic chemistry of silicon is deeply indebted. More recent interest has arisen for the most part in the laboratories of industrial institutions, but in the beginning there was Frederick S. Kipping of England.

It is true that Kipping referred to other workers in this field, mostly continental, who came before him; but these were few and their efforts were not always coordinated save when issuing from some one laboratory.

To Kipping then we may turn for the first organized series of papers relative to organic compounds of silicon, the theme of which, at least in the earlier days of his activity, centered around the hope of preparing compounds with asymmetric silicon, thus being resolvable enantiomorphs.

Kipping's first recorded publication on the subject of organic compounds of silicon appeared in 1899[368] in collaboration with L. L. Lloyd. It was noted in this paper that while preparing tetraphenylsilane by the method of Polis[68, 71, 72] a by-product was formed, melting at 148°, which was probably triphenylhydroxysilane. This compound reacted with acetyl chloride to form triphenylacetoxysilane; and when dissolved in acetic acid and warmed with nitric acid it underwent dehydration to form hexaphenyldisiloxane.

Kipping's first numbered paper[1] opened with a discussion of the preparation and properties of triphenylchlorosilane:

$$SiCl_4 + 3C_6H_5Cl + 6Na \rightarrow 6NaCl + (C_6H_5)_3SiCl$$
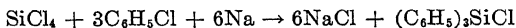
A hydrolysis product of this compound proved to be triphenylhydroxysilane. The presence of so many phenyl groups per molecule suggested nitration. However, the action of nitric acid on triphenylhydroxysilane produced only the ether, although with considerable ease:
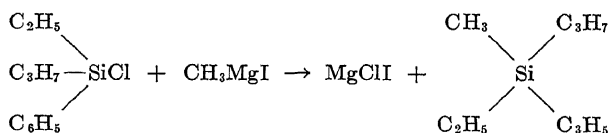
$$2(C_6H_5)_3SiOH \ (HONO_2) \rightarrow HOH + (C_6H_5)_3SiOSi(C_6H_5)_3$$
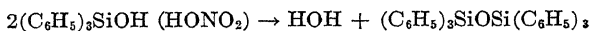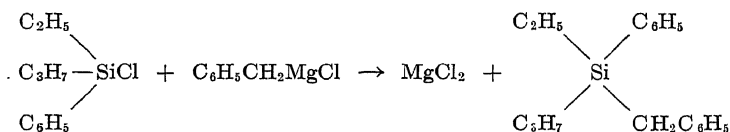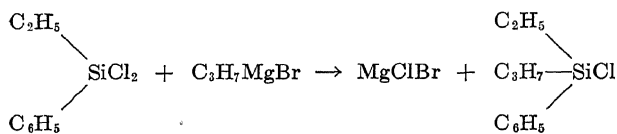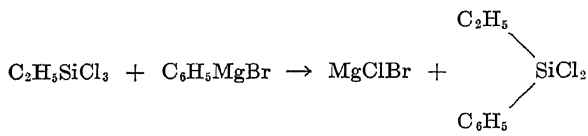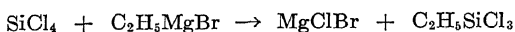
As a matter of fact, Kipping found that other reagents would do the same,

principally 10 per cent hydrochloric acid in acetic acid. This ether was easily hydrolyzed under the influence of boiling alcoholic potassium hydroxide. There must have been some diphenyldichlorosilane among the monochloro product because Kipping also found polymerized diphenyloxosilane as a hydrolysis product. Tetraethylsilane was also prepared:
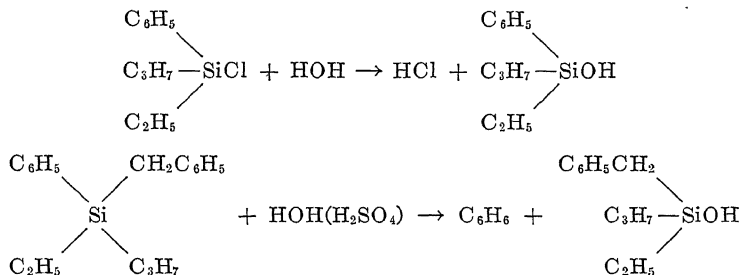
$$SiCl_4 + 4C_2H_5Br + 8Na \rightarrow 4NaBr + 4NaCl + (C_2H_5)_4Si$$
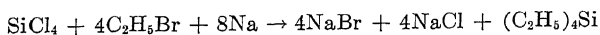
In 1904, Kipping[367] presented results covering the action of the Grignard reagent on tetrachlorosilane. Ethylmagnesium iodide gave all four possible products, ethyltrichlorosilane, diethyldichlorosilane, triethylchlorosilane, and tetraethylsilane. Ethyltrichlorosilane reacted with phenylmagnesium bromide to give ethylphenyldichlorosilane, and this with propylmagnesium bromide formed ethylphenylpropylchlorosilane. An equimolar mixture of tetrachlorosilane and ethylmagnesium bromide gave almost exclusively ethyltrichlorosilane. Ethylphenyldichlorosilane hydrolyzed to ethylphenyloxosilane.

Three years later, in 1907, Kipping[2] shifted his attention to the Grignard reagent in earnest, as a means to similar ends:

$$SiCl_4 + C_2H_5MgBr \rightarrow MgClBr + C_2H_5SiCl_3$$

$$C_2H_5SiCl_3 + C_6H_5MgBr \rightarrow MgClBr + \underset{C_6H_5}{\overset{C_2H_5}{\diagdown}}SiCl_2$$

$$\underset{C_6H_5}{\overset{C_2H_5}{\diagdown}}SiCl_2 + C_3H_7MgBr \rightarrow MgClBr + \underset{C_6H_5}{\overset{C_2H_5}{\diagdown}}C_3H_7{-}SiCl$$

$$\underset{C_6H_5}{\overset{C_2H_5}{\diagdown}}C_3H_7{-}SiCl + C_6H_5CH_2MgCl \rightarrow MgCl_2 + \underset{C_3H_7\quad CH_2C_6H_5}{\overset{C_2H_5\quad C_6H_5}{\diagdown\diagup}}Si$$

$$\underset{C_6H_5}{\overset{C_2H_5}{\diagdown}}C_3H_7{-}SiCl + CH_3MgI \rightarrow MgClI + \underset{C_2H_5\quad C_3H_7}{\overset{CH_3\quad C_3H_7}{\diagdown\diagup}}Si$$
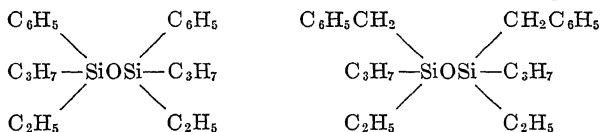
Judging from the comments in this article, it would seem that a considerable number and quantity of by-products accompanied all these preparations.

After isolation and purification of the various chlorides and radical-substituted silanes, he carried out the following reactions:
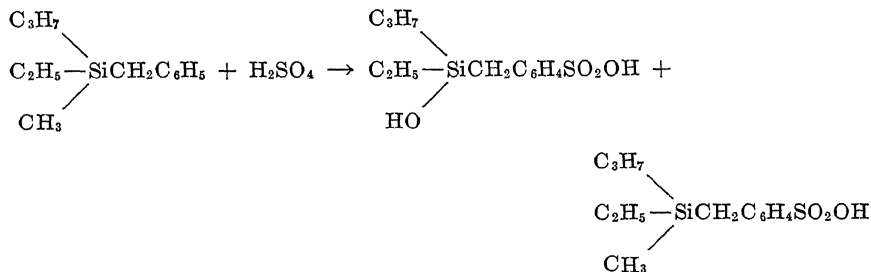
$$\underset{\underset{C_2H_5}{}}{\overset{\overset{C_6H_5}{}}{C_3H_7-SiCl}} + HOH \rightarrow HCl + \underset{\underset{C_2H_5}{}}{\overset{\overset{C_6H_5}{}}{C_3H_7-SiOH}}$$

$$\underset{\underset{C_2H_5}{}\quad\overset{}{}\ C_3H_7}{\overset{C_6H_5}{}\ \overset{}{}\ CH_2C_6H_5}{Si} + HOH(H_2SO_4) \rightarrow C_6H_6 + \underset{\underset{C_2H_5}{}}{\overset{\overset{C_6H_5CH_2}{}}{C_3H_7-SiOH}}$$

Both of these hydroxides passed over spontaneously to the corresponding oxides or ethers:

$$\underset{\underset{C_2H_5}{}\quad\underset{C_2H_5}{}}{\overset{\overset{C_6H_5}{}\quad\overset{C_6H_5}{}}{C_3H_7-SiOSi-C_3H_7}} \qquad \underset{\underset{C_2H_5}{}\quad\underset{C_2H_5}{}}{\overset{\overset{C_6H_5CH_2}{}\quad\overset{CH_2C_6H_5}{}}{C_3H_7-SiOSi-C_3H_7}}$$

Sulfuric acid acting on benzylethylpropylhydroxysilane produced a mixture of sulfonic acids, isolated as ammonium salts. From 1,3-dibenzyl-1,3-diethyl-1,3-dipropyldisiloxane a monosulfonic acid was isolated with the sulfonic acid group attached to a nuclear carbon of the benzyl group. Derivatives of this acid were prepared as follows: menthylamine salt, bornyl ester, strychnine salt and cinchonine salt. Satisfactory results were not always obtained here in the study of the optical activity of some of these products, although the rotatory power of *dl* acids after combination with *l*-alkaloids could be determined.

In the same year appeared Kipping's third contribution[3] continuing the investigation of the action of sulfuric acid on tetra-substituted silanes. By this reaction, but more easily by the use of chlorosulfonic acid, Kipping eventually prepared the *l*-menthyl and ammonium salts of the following two products:

$$\underset{\underset{CH_3}{}}{\overset{\overset{C_3H_7}{}}{C_2H_5-SiCH_2C_6H_5}} + H_2SO_4 \rightarrow \underset{\underset{HO}{}}{\overset{\overset{C_3H_7}{}}{C_2H_5-SiCH_2C_6H_4SO_2OH}} +$$

$$\underset{\underset{CH_3}{}}{\overset{\overset{C_3H_7}{}}{C_2H_5-SiCH_2C_6H_4SO_2OH}}$$
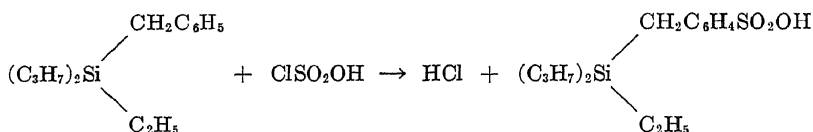
It seems as though the formation of the hydroxysilane were the result of a second (consecutive) reaction as the methyl derivative was also isolated, as shown above. This second reaction was probably akin to hydrolysis, as methane was the by-product.

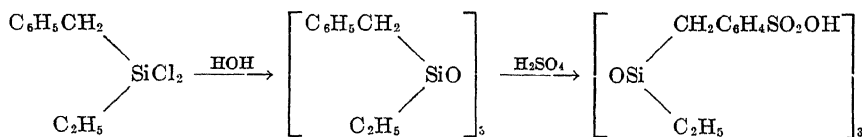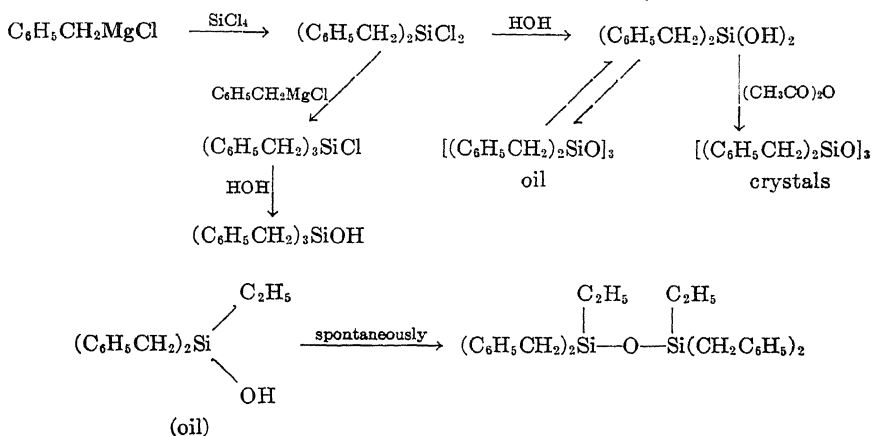Compounds used in this work were synthesized as follows:

$$C_2H_5SiCl_3 \xrightarrow{\ C_6H_5CH_2MgCl\ } \underset{C_2H_5}{\overset{C_6H_5CH_2}{>}}SiCl_2 \xrightarrow{\ HOH\ } \underset{C_2H_5}{\overset{C_6H_5CH_2}{>}}SiO$$

(probably a polymer)

$C_3H_7MgCl \downarrow$

$$\underset{\underset{CH_3}{C_2H_5}}{\overset{\overset{C_6H_5CH_2}{C_3H_7}}{>}}Si \xleftarrow{\ C_3H_7MgCl\ } \underset{C_2H_5}{\overset{C_6H_5CH_2}{>}}C_3H_7{-}SiCl \xrightarrow{\ HOH\ } \underset{C_2H_5}{\overset{C_6H_5CH_2}{>}}C_3H_7{-}SiOH$$

$p\text{-}CH_3C_6H_4NH_2 \swarrow \qquad\qquad spontaneously \swarrow \qquad H_2SO_4 \downarrow$

$$\underset{C_2H_5}{\overset{C_6H_5CH_2}{>}}C_3H_7{-}SiNHC_6H_4CH_3 \qquad \left[\underset{C_2H_5}{\overset{C_6H_5CH_2}{>}}C_3H_7{-}Si \right]_2 O \qquad \underset{HO}{\overset{C_3H_7}{>}}C_2H_5{-}SiCH_2C_6H_4SO_2OH$$
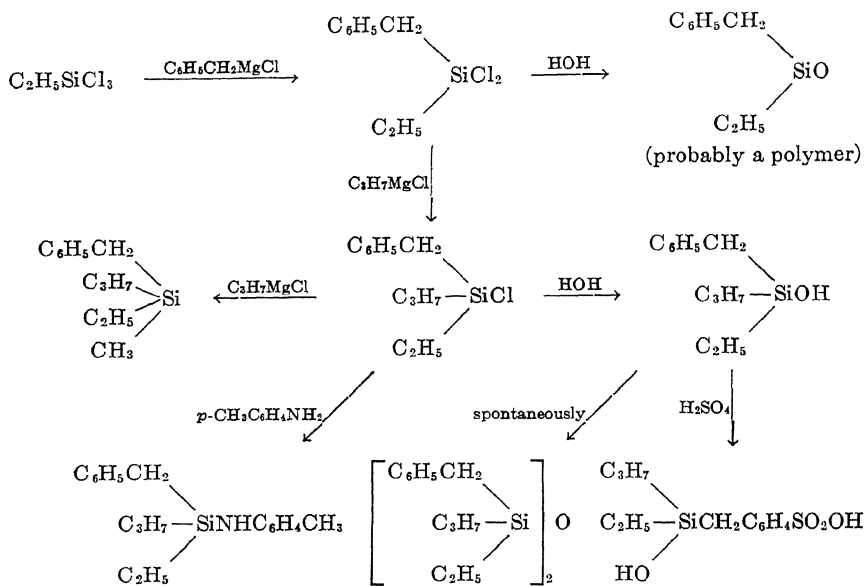
Other sulfonic acids were later prepared (4):

$$\underset{C_2H_5}{\overset{CH_2C_6H_5}{(C_3H_7)_2Si}} + ClSO_2OH \rightarrow HCl + \underset{C_2H_5}{\overset{CH_2C_6H_4SO_2OH}{(C_3H_7)_2Si}}$$

Alkaloidal salts of this acid resembled, generally speaking, the salts previously reported. Other compounds prepared by standard methods were diphenylethylchlorosilane, 1,1,3,3-tetraphenyl-1,3-diethyldisiloxane, ethyltriphenylsilane and methyltriphenylsilane.

In the same year appeared the report of work on the hydrolysis of benzylethyldichlorosilane[5]:

$$\underset{C_2H_5}{\overset{C_6H_5CH_2}{>}}SiCl_2 \xrightarrow{\ HOH\ } \left[\underset{C_2H_5}{\overset{C_6H_5CH_2}{>}}SiO \right]_3 \xrightarrow{\ H_2SO_4\ } \left[\underset{C_2H_5}{\overset{CH_2C_6H_4SO_2OH}{OSi}} \right]_3$$

$$C_6H_5CH_2MgCl \xrightarrow{\text{SiCl}_4} (C_6H_5CH_2)_2SiCl_2 \xrightarrow{\text{HOH}} (C_6H_5CH_2)_2Si(OH)_2$$

$$C_6H_5CH_2MgCl \swarrow \qquad \diagup\diagup \qquad \Big\downarrow (CH_3CO)_2O$$

$$(C_6H_5CH_2)_3SiCl \qquad [(C_6H_5CH_2)_2SiO]_3 \qquad [(C_6H_5CH_2)_2SiO]_3$$
$$\text{HOH}\Big\downarrow \qquad\qquad\qquad \text{oil} \qquad\qquad\qquad \text{crystals}$$
$$(C_6H_5CH_2)_3SiOH$$

$$(C_6H_5CH_2)_2Si\diagup^{\displaystyle C_2H_5}_{\diagdown OH} \xrightarrow{\text{spontaneously}} (C_6H_5CH_2)_2Si\overset{\displaystyle C_2H_5}{|}-O-\overset{\displaystyle C_2H_5}{|}Si(CH_2C_6H_5)_2$$

(oil)

Trimeric benzylethyloxosilane had very little in common with ketones of the carbon series. Hydrogen, hydroxylamine and hydrazine did not react. Its trimeric nature was ascertained by molecular weight determinations.

1,3-Dibenzyl-1,3-diethyl-1,3-dipropyldisiloxane[6] was also prepared and sulfonated and the optical properties of the resulting sulfonic acid determined. This sulfonic acid reacted with sodium hydroxide to give sodium *p*-toluene sulfonate. Similar compounds containing the isobutyl group were also prepared:

$$\overset{\displaystyle C_6H_5CH_2\diagdown}{\underset{\displaystyle C_2H_5\diagup}{}}SiCl_2 \xrightarrow{i\text{C}_4\text{H}_9\text{MgI}} \overset{\displaystyle C_6H_5CH_2\diagdown}{\underset{\displaystyle C_2H_5\diagup}{i\text{C}_4\text{H}_9-}}SiCl \xrightarrow{\text{HOH + Na}_2\text{CO}_3} \overset{\displaystyle C_6H_5CH_2\diagdown}{\underset{\displaystyle C_2H_5\diagup}{i\text{C}_4\text{H}_9-}}SiOH$$

$$\text{ClSO}_2\text{OH}\diagdown \qquad\qquad\qquad \Big\downarrow$$

$$\left[\overset{\displaystyle HOSO_2C_6H_4CH_2\diagdown}{\underset{\displaystyle C_2H_5\diagup}{i\text{C}_4\text{H}_9-}}Si\right]_2 O \xleftarrow{\text{ClSO}_2\text{OH}} \left[\overset{\displaystyle C_6H_5CH_2\diagdown}{\underset{\displaystyle C_2H_5\diagup}{i\text{C}_4\text{H}_9-}}Si\right]_2 O$$
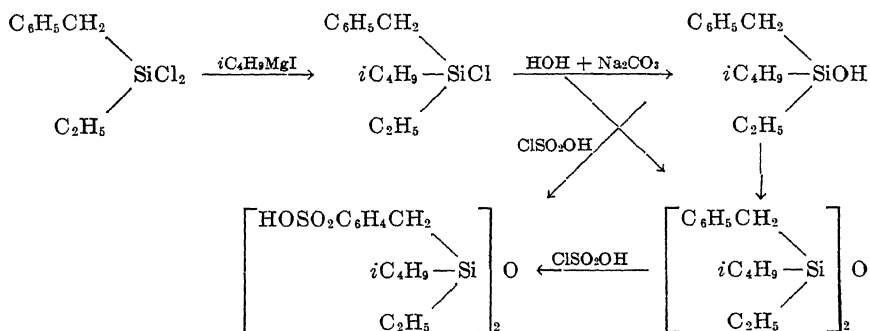
The optical properties of this sulfonic acid were studied through the media of various alkaloidal salts[7, 8]. Isobutylmagnesium chloride[9] was found to react with benzylethylpropylchlorosilane only at 140°. The product was benzylethylisobutylpropylsilane. This compound was then sulfonated on the aromatic ring and the optical properties of the alkaloidal salts of this sulfonic acid were likewise made the objects of study.

Martin and Kipping[10] surveyed most of the work to date and presented

several generalizations as well. It was observed that many reagents sufficed to dehydrate R_3SiOH to the corresponding ether, including alcoholic hydrochloric acid. Benzoyl and acetyl chlorides converted the silanol to the chloride:

$$(C_6H_5CH_2)_3SiOH + CH_3COCl \rightarrow (C_6H_5CH_2)_3SiCl + CH_3COOH$$
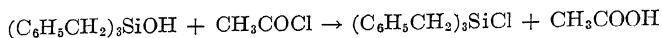
Surely this reaction would seem to present evidence against the tendency of these hydroxysilanes uniformly to ionize or otherwise split in the acid sense. In fact this type of reaction seems at first glance to put them definitely in the category of the tertiary carbon alcohols, which react with acid halides in the same manner. Martin and Kipping believed that the dehydration of a tertiary silanol to the ether proceeds through the intermediate formation of the chloride, and then the reaction of this chloride with more silanol, in spite of the apparent necessity which this reaction calls forth of assuming acid splitting or ionization of the second molecule of silanol. Indeed the equation given above may take an entirely different course

$$(C_6H_5CH_2)_3SiOH + CH_3COCl \rightarrow HCl + CH_3COOSi(CH_2C_6H_5)_3,$$

$$CH_3COOSi(CH_2C_6H_5)_3 + HCl \rightarrow (C_6H_5CH_2)_3SiCl + CH_3COOH$$
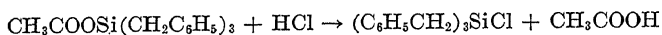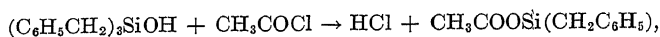
Splitting of the ester between silicon and oxygen might be more logical, and splitting of the silanol between oxygen and hydrogen would be more in accordance with the equation given previously in connection with another reference[368]. There is still the possibility that the phenyl groups attached to silicon in the older reference[368] may have induced a reaction entirely different from that which occurred with benzyl groups in place[10].

Another hydrolysis was carried out on diethyldichlorosilane[10] with water. An oil of the consistency of glycerol was formed; when suitably dried this showed a molecular weight of 604. It was therefore approximately a hexamer. When dried again, this product was soluble in ether, benzene and acetone.

Later, Kipping and Martin[11] repeated the work of Ladenburg[76] in which the latter claimed to have successfully sulfonated triphenylhydroxysilane. Kipping and Martin were able to isolate only benzene sulfonic acid and phenylene disulfonic acid.

Dibenzylethylchlorosilane[12] has been prepared by mixing ethyltrichlorosilane and magnesium and dropping benzyl chloride into the mixture. The product was an oil having a bluish-violet fluorescence and a rather pungent odor; it gave off fumes in moist air and reacted rapidly with water. When treated with propylmagnesium bromide the oil gave dibenzylethylpropylsilane. Adding chlorosulfonic acid to a chloroform solution of dibenzylethylpropylsilane caused the formation of mono and disulfonic

acids the optical properties of which were studied through the medium of their alkaloidal salts. It was also claimed[13] that the action of sodium on ethylphenyldichlorosilane formed a compound 1,2-diethyl-1,2-diphenyl-silene having a double bond between two silicon atoms:

$$2 \quad \underset{C_2H_5}{\overset{C_6H_5}{\diagdown}} SiCl_2 + 4Na \rightarrow 4NaCl + \underset{C_2H_5}{\overset{C_6H_5}{\diagdown}} Si{=}Si \underset{C_6H_5}{\overset{C_6H_5}{\diagup}} \quad (?)$$
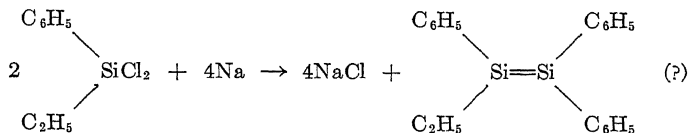
A more probable reaction was also reported:

$$2(C_6H_5)_3SiCl + 2Na \rightarrow 2NaCl + (C_6H_5)_3SiSi(C_6H_5)_3$$

This was followed by an investigation into the optical properties of the monosulfonic acid of dibenzylethylpropylsilane[14].

Kipping and Hackford[15] noticed the similarities and dissimilarities between monomeric silicones and carbon ketones and the question apparently arose as to just how far the similarities would extend. Specifically, would these silicones, trimers and tetramers though they may be, react with the Grignard reagent as do the carbon ketones?

In the first place it was discovered that hexa-substituted disiloxanes did not react with the Grignard reagent and that, in full accord with the processes of carbon chemistry, C_6H_5SiOOH and $C_6H_5CH_2SiOOH$ formed tertiary alcohols:

$$C_6H_5SiOOH + 2C_6H_5MgBr \rightarrow MgO + MgBr_2 + (C_6H_5)_3SiOH$$
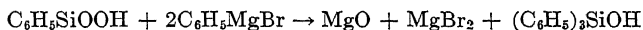
The silicones also reacted as if they were monomeric carbon ketones:

$$\left[\underset{C_2H_5}{\overset{C_6H_5CH_2}{\diagdown}}SiO\right]_3 + 3C_2H_5MgBr \text{ (followed by} \rightarrow \text{hydrolysis)} \quad \underset{C_2H_5}{\overset{C_6H_5CH_2}{\diagdown}} C_6H_5{-}SiOH$$
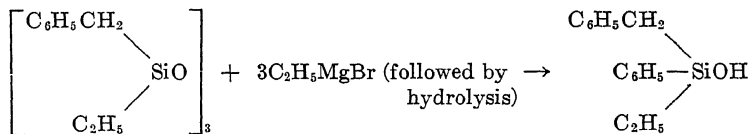
Does this constitute evidence for the reversible association and cyclization of oxosilanes and if so, are these compounds depolymerized by the Grignard reagent acting catalytically? The hydroxysilane quickly and spontaneously passed over to the corresponding oxide, and with acetyl chloride formed benzyldiethylchlorosilane in 5 per cent yield. The same reaction was observed with monomeric dibenzyldihydroxysilane. Substituting propylmagnesium bromide for ethylmagnesium bromide in the equation presented above caused the formation of benzylethylpropylhydroxysilane, and in a similar manner dibenzylmethylhydroxysilane and benzylethylmethylhydroxysilane were also prepared. The first of these readily formed

the oxide by loss of one molecule of water from two molecules of the hydroxysilane.

The work covered in this paper can be summarized as follows:

$$
\begin{array}{c}
C_6H_5CH_2 \\
\diagdown \\
\quad\quad SiCl_2 \\
\diagup \\
C_2H_5
\end{array}
\xrightarrow{HOH}
\begin{array}{c}
C_6H_5CH_2 \\
\diagdown \\
\quad\quad SiO \\
\diagup \\
C_2H_5
\end{array}
\xrightarrow{C_2H_5MgBr}
\xrightarrow{HOH}
\begin{array}{c}
C_6H_5CH_2 \\
\diagdown \\
C_2H_5 - SiOH \\
\diagup \\
C_2H_5
\end{array}
$$

$$
\left| C_3H_7MgBr \right.
$$

$$
\left| HOH \right.
$$

$$
\begin{array}{c}
C_6H_5CH_2 \\
\diagdown \\
C_3H_7 - SiOH \\
\diagup \\
C_2H_5
\end{array}
\qquad\qquad
CH_3COCl \Big|
$$

$$
\left[
\begin{array}{c}
C_6H_5CH_2 \\
\diagdown \\
C_2H_5 - Si - \\
\diagup \\
C_2H_5
\end{array}
\right]_2 O
$$
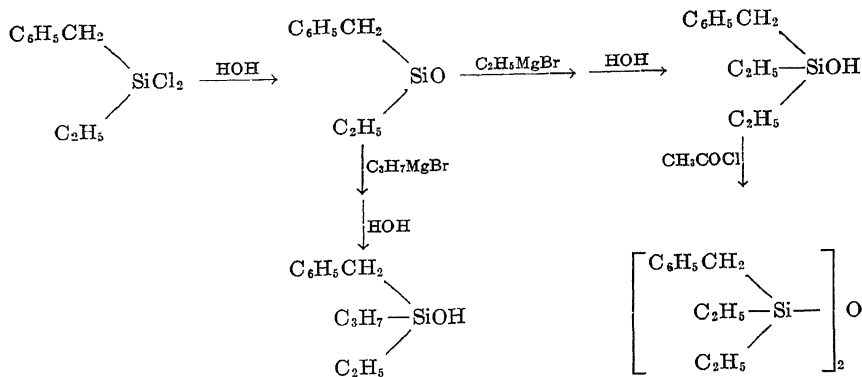
In similar fashion there were prepared ethylmethylphenylhydroxysilane and diethylphenylhydroxysilane. Then in addition was formed:

$$
[(C_6H_5CH_2)_2SiO]_3 \xrightarrow{CH_3MgBr} \xrightarrow{HOH}
\begin{array}{c}
C_6H_5CH_2 \\
\diagdown \\
C_6H_5CH_2 - SiOH \\
\diagup \\
CH_3
\end{array}
\rightarrow
\left[
\begin{array}{c}
C_6H_5CH_2 \\
\diagdown \\
C_6H_5CH_2 - Si - \\
\diagup \\
CH_3
\end{array}
\right]_2 O
$$
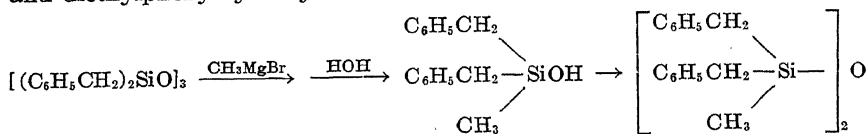
Dibenzyldihydroxysilane, treated in the same manner gave the same products.

The net result of this work seems to be that evidence has been presented to show that many of these organic compounds of silicon have a chemistry closely parallel to those of carbon in spite of conditions of nuclear size, relative electronegativity, etc.

A paper concerning the nomenclature of organic compounds of silicon followed in chronological order[16].

Workable laboratory directions for the preparation of certain phenylchlorosilanes were presented in the same year[17]. Kipping here used the method of Dilthey and Eduardoff[74], though modified to fit his own needs and for greater efficiency. In this manner were prepared phenyltrichlorosilane, diphenyldichlorosilane and triphenylchlorosilane, the last being a solid. Diphenyldihydroxysilane was found not to melt without decomposition. With respect to this compound, however, an occasional melting point of 160° was reported, due perhaps to dimorphism. It began to sinter at 125°, melting as mentioned above with decomposition from 128° to 132°. The hydrolysis of diphenyldichlorosilane[18] was carried out by the action of cold concentrated ammonium hydroxide; this produced an oil which on distillation formed 1,1,3,3-tetraphenyl-1,3-dihydroxydisiloxane.

This ether, when heated over a free flame, passed over to the trimer, some going even farther to the tetramer. These derivatives were probably cyclic in nature, as perhaps

$$C_6H_5SiC_6H_5$$

$$(C_6H_5)_2Si \qquad Si(C_6H_5)_2$$
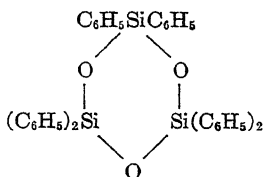
The tetramer was also formed by the action of acetyl chloride. Another product of the above distillation was 1,1,3,3,5,5-hexaphenyl-1,5-di-hydroxytrisiloxane.

A better method for preparing the cyclic trimer was evolved by heating the diphenyldihydroxysilane first at 150° then at 180° to theoretical weight. The product showed a melting point of 188° to 189°, but the molecular weight as determined in benzene was abnormal. Kipping believed that this cyclic silicone or oxosilane was identical with Dilthey's "termolecular silicone"[75]. All of the above three compounds were also prepared by the action of traces of acid or alkali on diphenyldihydroxysilane.

Robison and Kipping[19] repeated these procedures, eventually preparing cyclic trimeric dibenzyloxosilane. Similar procedures of hydrolysis[20] applied to ethylphenyldichlorosilane gave ethylphenyldihydroxysilane, in long needles. With a few drops of concentrated HCl, this compound was converted to 1,3-diethyl-1,3-dihydroxy-1,3-diphenyldisiloxane. Benzyl-phenyldihydroxysilane was easily dehydrated to an oil. Benzylethyldi-hydroxysilane was also prepared. Later, Smith and Kipping[21] compared the properties of organic compounds of silicon with corresponding compounds of tin. Condensations of dibenzyldihydroxysilane[22] were continued with the formation of
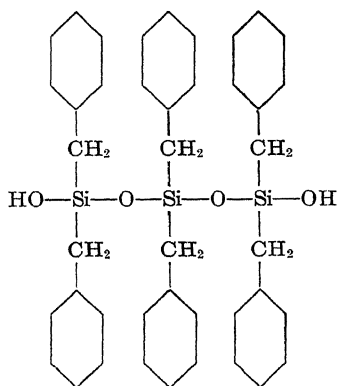
By this time, the suspicion had apparently arisen in the minds of Kipping and others that the heat dehydration of compounds such as diphenyldihydroxysilane did not proceed by any simple mechanism. Consequently Kipping and Robison studied in considerable detail the dehydration under various conditions of phenyltrihydroxysilane[23, 24, 584, 585] and of benzyltrihydroxysilane[26].

Interspersed chronologically with these three papers appeared a comment on a contribution by Martin in which Kipping[25] pointed out the fact that Martin's method[79] for the preparation of tetrachlorosilane had originated with Warren[339].

Taking diphenyldihydroxysilane as an example, the reactions reported in the last three papers[23, 24, 25] may be formulated as follows:
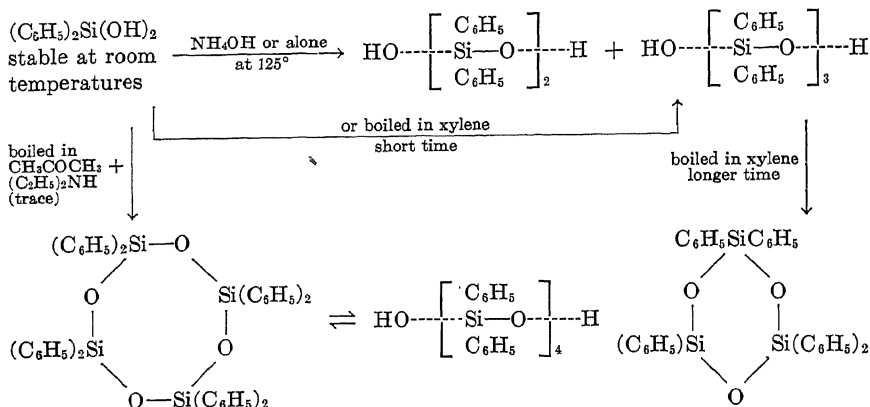
The ease with which this type of condensation was carried out aroused the suspicion that another end product, C_6H_5SiOOH, was not a "simple compound." Hydrolysis of phenyltrichlorosilane led to the isolation of five glue-like fractions believed to be various hydration products of the simple acid. Results starting with benzyltrichlorosilane were analogous.

Returning to his study of optical activity among silicon compounds, Kipping[27] in 1921 presented data on the preparation and resolution of derivatives of ethylphenylpropylchlorosilane. This compound was treated with metallic sodium in dry xylene. The organic product was a mixture, boiling over a wide range of temperatures. However, there was obtained a viscous liquid with a pleasant odor, somewhat aromatic, slightly volatile with steam, decomposable with bromine and with concentrated sulfuric acid at 100° giving, in the latter case, benzene. The pure disilane boiled at 244° to 248° (20 mm). This product was a moderately mobile liquid, miscible with most organic solvents, and relatively stable toward alkalies.

It reacted with concentrated sulfuric acid to give a disulfonate. Kipping wrote the following equations:

$$
\begin{matrix}
C_6H_5 & & C_6H_5 & & & & HO & & OH \\
& \diagdown & \diagup & & & & & \diagdown & \diagup \\
C_3H_7 & -SiSi- & C_3H_7 & + 2HOH(H_2SO_4) \longrightarrow 2C_6H_6 + & C_3H_7 & -SiSi- & C_3H_7 \\
& \diagup & \diagdown & & & & & \diagup & \diagdown \\
C_2H_5 & & C_2H_5 & & & & C_2H_5 & & C_2H_5
\end{matrix}
$$

$$
\begin{matrix}
C_6H_5 & & C_6H_5 & & & HOSO_2C_6H_4 & & C_6H_4SO_2OH \\
& \diagdown & \diagup & & & & \diagdown & \diagup \\
C_3H_7 & -SiSi- & C_3H_7 & + 2H_2SO_4 \longrightarrow 2HOH + & C_3H_7 & -SiSi- & C_3H_7 \\
& \diagup & \diagdown & & & & \diagup & \diagdown \\
C_2H_5 & & C_2H_5 & & & C_2H_5 & & C_2H_5.
\end{matrix}
$$
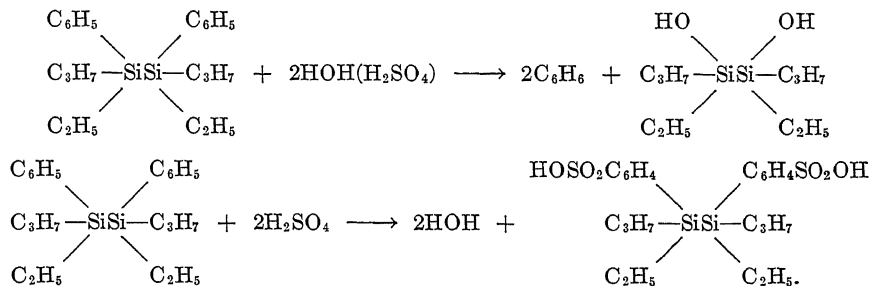
In the same year, work was reported leading eventually to rather interesting conclusions concerning the possibility of the existence of free radicals in the silicon series. Kipping's twenty-fifth paper[28] (his own numbers) recorded the action of sodium on diphenyldichlorosilane. From the understandably complex mixture there were isolated two compounds of the formula $Si_4(C_6H_5)_8$, no reasons being assigned for this apparent isomerism. These compounds were soluble in benzene and toluene. Octaphenyltetrasilane underwent many addition reactions, for instance with iodine, giving octaphenyldiiodotetrasilane, stable up to 250°. In fact, this octaphenyltetrasilane could actually be titrated against iodine. It reacted with ammonium hydroxide in acetone, giving about a 15 per cent yield of a gluey material, $(C_6H_5)_8Si_4O$. The melting point of this product varied with the manner of heating in connection with the melting point determination—fast, slow or intermediate. Boiling nitrobenzene oxidized the compound to $(C_6H_5)_8Si_4O_2$.

In connection with this work there will also be found a paper[29] describing the release of hydrogen by the action of pyridine on certain silico organic compounds. It was assumed that the reaction proceeded as follows:

$$(C_6H_5)_8Si_4 + 8HOH \rightarrow 4H_2 + 4(C_6H_5)_2Si(OH)_2$$
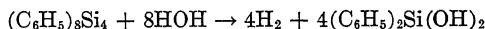
Strictly speaking, this was not dehydrogenation in this particular case, but rather a reaction with water, the hydroxyls splitting the silicon chains and hydrogen being given off. Later examples constituted true dehydrogenations, since part of the hydrogen evolved actually came from the silicon compound. Several compounds were worked up, however, with quite satisfactory agreement between experimental and theoretical hydrogen evolved.

In 1923 Kipping published his twenty-seventh article in the series entitled "A Probable Example of Tervalent Silicon."[30]

Octaphenyltetrasilane is indeed a novel compound, if for no other reason than its properties. In the first place Kipping found it relatively stable in air, turning yellow only with time, but oxidizable simply by the action of boiling toluene or when heated at 100° for any length of time. The benzene solution decomposed rapidly under reflux, but the solution in diphenyl was much more stable. Oxygen compounds, such as benzyl alcohol, acetophenone or amyl nitrite, caused decompositon, probably by transfer of oxygen. Ozone naturally did the same. Organic chlorides, *e.g.*, acetylene tetrachloride and ethylene dichloride as well as bromobenzene, reacted with octaphenyltetrasilane, yielding compounds which after hydrolysis were found to include $(C_6H_5)_8Si_4O$ and $(C_6H_5)_4SiO_2$. PCl_3 did likewise. Hydrobromic acid had no action, nor had diphenyldichlorosilane in toluene, but the latter without solvent turned the substituted silane to a glue. At this point Kipping suggested a very logical formula for the compound in view of its extreme reactivity:

$$\begin{array}{cccc} C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5 \\ | & | & | & | \\ -Si----Si----Si----Si- \\ | & | & | & | \\ C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5 \end{array}$$
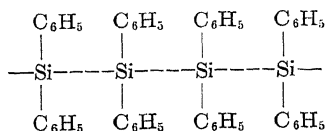
The iodine addition product of octaphenyltetrasilane[31] reacted with a standard Grignard reagent:

$$(C_6H_5)_8Si_4I_2 + C_2H_5MgBr \rightarrow [(C_6H_5)_8Si_4(C_2H_5)_2](HOH)_3$$
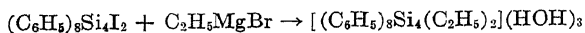
This product was opaque at 120°, melting at 253°–254°. A by-product here was $(C_6H_5)_8Si_4O$. A 5 per cent aqueous solution of NaOH had no effect on the product of the above reaction, but the addition of piperidine caused a drop in hydrogen content. Octaphenyldiiodotetrasilane lost all its iodine on contact with sodium.

The twenty-ninth paper in order[32] concerned itself with a return to the study of hydrolysis and dehydration. *p*-Tolyltrichlorosilane was prepared through the medium of the proper Grignard reagent. This compound reacted with water giving some sort of polymerized product corresponding to the monomeric formula $CH_3C_6H_4SiOOH$. The other silicon product proved to be di-*p*-tolyldichlorosilane. As this compound fumed only slightly in moist air, the authors considered it somewhat contaminated in spite of its definite boiling point. This reservation seems to have been a bit of rather excessive modesty on Kipping's part. The average overall yield amounted to 23 per cent and was not materially increased by continued modification of the process. Di-*p*-tolyldihydroxysilane was heated at 100°

for three hours, whereupon water was lost, forming a compound which was probably:
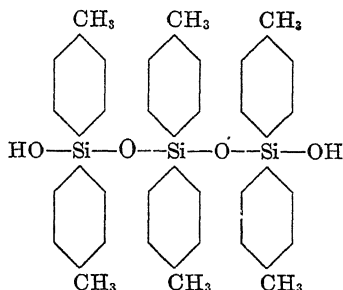
The same end was attained using HCl and CH_3COOH as solvent and allowing the solution to stand exposed to the air for a time. At 150° this dihydroxy compound cyclized, forming dodeca-*p*-tolylcyclohexasiloxane with loss of water. When heated with an acetone solution of piperidine, di-*p*-tolyldihydroxysilane formed $C_{56}H_{56}Si_4O_4$, probably also a cyclic compound, with alternate silicons and oxygens.

Kipping's thirtieth paper[33] opened with a summary of certain phases of his work already reported. A restatement will be found here of the fact that the action of sodium on diphenyldichlorosilane[28] resulted in the formation of several different compounds. Two of these of the formula $(C_6H_5)_8Si_4$ were isolated, one of which had been shown to have properties indicating its existence as a linear free radical; the other, somewhat more innert, probably exists in cyclic form. Then two more were described: the first of these $[(C_6H_5)_2Si]_n$, with n having a value of 6 or 8, because of its low reactivity was assumed to be cyclic in nature; the other, of the same general formula, with an undetermined value for n resembled a free radical in its properties.

In the same year, Vyle and Kipping[34] presented the results of certain investigations on the action of a selected group of metallic oxides on organo silicon halides or organo halogenated silanes. Most of their attention was directed to the action of mercuric oxide. In boiling toluene from one to two hours, mercuric oxide reacted with diphenyldichlorosilane to give a precipitate of a miscellaneous group of products, mostly inorganic. From the toluene-soluble portion of the residue small amounts of hexaphenyl-cyclotrisiloxane were isolated. This was a crystalline solid, recrystallizable from an alcohol-acetone mixture. The same compound also showed up as an octamer (an oil); the molecular weight of the latter compound, the octamer, was determined in benzene solution. Similarly, dibenzyldichlorosilane reacted with mercuric oxide to form the cyclic trimer, but

nothing of higher molecular weight. Silver oxide and cadmium oxide did not react with diphenyldichlorosilane.

Kipping's thirty-second paper[35] presented comments on a portion of Schlenk's work[32] in which the latter claimed to have isolated diphenylmethylenylsilane as a result of the action of methylmagnesium chloride on diphenyldichlorosilane, with loss of hydrochloric acid. Repeating this procedure, Kipping obtained none of Schlenk's product, but his results bore out the assumption that diphenylmethylhydroxysilane was formed, and that it slowly dehydrated to the oxide. Dimethyldiphenylsilane was also formed (a liquid). Tribenzylchlorosilane could not be made to lose hydrochloric acid to give Schlenk's compound even when heated with dimethylaniline or quinoline. Tribenzylhydroxysilane was unaffected by boiling acetic anhydride or by P_2O_5 or $ZnCl_2$. Kipping concluded that the formation of Si$=$C linkages is extremely improbable.

The action of metallic sodium on organochlorosilanes continued to absorb the interest of Kipping and his co-workers[36]. The thirty-third numbered contribution presented factors showing that the glue-like, very soluble product of the action of sodium on diphenyldichlorosilane was mostly amorphous cyclic octaphenyltetrasilane. It was suggested that the "glue" consisted of molecules of the tetrasilane so entangled during formation that they were inseparable, or nearly so.

Diphenyldichlorosilane reacted with phenol in benzene[37]. As a matter of fact Kipping and Murray[38] found that even diethyl ether reacted with tetrachlorosilane at room temperatures to a slight extent. Potassium hydroxide reacted with diphenyldichlorosilane and with di-p-tolyldichlorosilane but did not produce concrete results[39]. In each case two products were obtained, one of an insoluble nature and the other more soluble, *e.g.*, in benzene. From diphenyldichlorosilane the soluble compound showed a molecular weight of about 3900 and from the corresponding p-tolyl compound, 4150. The molecular weight of the insoluble product from di-p-tolyldichlorosilane was 3450.

When sodium was reacted with dibenzyldichlorosilane[40] in toluene under an atmosphere of nitrogen, with subsequent addition of a small percentage of potassium, small amounts of hexabenzyldisiloxane and tetrabenzylsilane were formed; but the main product was a thick oil analyzing as octabenzyltetrasilane monoxide or $(C_6H_5CH_2)_8Si_4O$. It was claimed that the oxygen was due to the presence of a little sodium oxide with the sodium.

$$(C_6H_5CH_2)_2SiCl_2 + 2Na \rightarrow C_6H_5CH_2Si(Na)Cl_2 + C_6H_5CH_2Na$$

$$(C_6H_5CH_2)_2SiCl_2 + 2C_6H_5CH_2Na \rightarrow 2NaCl + (C_6H_5CH_2)_4Si$$

$$(C_6H_5CH_2)_2SiCl_2 + C_6H_5CH_2Na \rightarrow NaCl + (C_6H_5CH_2)_3SiCl$$

$$2(C_6H_5CH_2)_2SiCl_2 + Na_2O \rightarrow 2NaCl + ((C_6H_5CH_2)_3Si)_2O$$
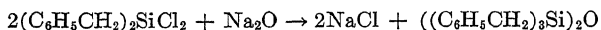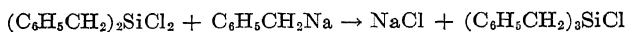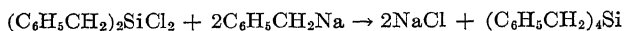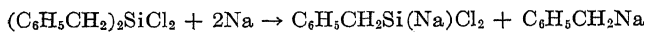
Tetrachlorosilane reacted with p-tolylmagnesium bromide[58] with the formation of tri-p-tolylchlorosilane. When treated with dilute ammonium hydroxide, this formed the corresponding hydroxy compound which, warmed with alcohol and sodium hydroxide, went over to the oxide [(p-$CH_3C_6H_4)_3Si]_2O$.

In 1928 there appeared two papers from Kipping's laboratories[55, 56] on topics not directly related to the series of investigations then in progress. In the first of these[55] the detection and separation of the titanium chlorides found in tetrachlorosilane was discussed. In the second[56] the action of tetrachlorosilane on dry ether was reported. From the distillate after reaction, the standard reagents formed a slight precipitate of iodoform.

Returning to the subject of highly phenylated polysilanes, it was found[41] that octaphenyltetrasilane, when destructively distilled, formed tetraphenylsilane as well as triphenylsilane, the latter being a liquid. There were also polymerized products with molecular weights ranging up to 4000. Linear octaphenyltetrasilane, when subjected to the same treatment, formed tetraphenylsilane and triphenylsilane but no cyclic compounds.

A bit of controversy seems to have been set up with regard to triphenylsilane. In 1907, Ladenburg[76] isolated a crystalline compound, m.p. 200°–203°, which he claimed was triphenylsilane. This product was but sparingly soluble in acetone and benzene. He was unable to obtain the compound in later attempts. Kipping here stated that he had isolated an oil which would not crystallize at 0°; this oil showed all the properties of triphenylsilane. The compound reduced potassium permanganate but did not add iodine; and although results of molecular weight determinations, combustions and silicon determinations were admittedly not definite as to whether the product was triphenylsilane or triphenylsilicyl, Kipping believed that its failure to react with iodine precluded the possibility of its being a free radical. Treatment with bromine gave hydrobromic acid immediately. The hydrogen value with alkalies did not agree with the theoretical for triphenylsilicyl:

$$2(C_6H_5)_3Si + 2HOH \rightarrow 2(C_6H_5)_3SiOH + H_2$$
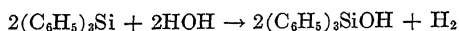
but rather with that for triphenylsilane:

$$(C_6H_5)_3SiH + HOH \rightarrow (C_6H_5)_3SiOH + H_2$$
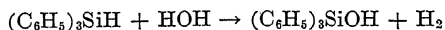
For a continuation of this discussion, the reader is referred to a listing of the work of Kraus[203].

Contribution thirty-nine[42] from the laboratories of Kipping combined the features of a continued investigation of the action of sodium on a chlorosilane with some additional attempts to prepare unusual compounds with Si-Si linkages, including the double bond. After all, few compounds

actually react with sodium to give isolable products with disilane linkages, and none have been prepared with double bonds between silicons. Diphenyldichlorosilane and diphenylphenoxychlorosilane did not prove very satisfactory in attempts to isolate new products. The work was continued[43] but without any more good fortune than previously, except that the action of sodium on phenyltrichlorosilane was found to give a quantitative yield of an unidentifiable powder when the reaction was carried out at 180°. The boiling point of phenyltrichlorosilane was given as 152° to 153° at 200 mm.

Di-*p*-tolyldichlorosilane was also treated with an excess of sodium[44] in dry toluene under an atmosphere of nitrogen. Two products were isolated, both linear and cyclic octa-*p*-tolyltetrasilane. Linear octa-*p*-tolyltetrasilane absorbed iodine forming $(CH_3C_6H_4)_8Si_4I_2$, melting at 300° with decomposition; this compound slowly turned brown in ether and in benzene. The original linear hydrocarbon also absorbed oxygen in dilute acetone solution to form $(CH_3C_6H_4)_8Si_4O$. Cyclic octa-*p*-tolyltetrasilane did not absorb iodine.

Palmer and Kipping[45] investigated the action of cyclohexylmagnesium bromide on tetrachlorosilane in dry ether. Cyclohexyltrichlorosilane was isolated. Hydrolysis of the product formed the conventional acid, cyclohexyloxohydroxysilane, which was found to dehydrate to 1,3-dicyclohexyl-1,3-dioxodisiloxane. In addition there was obtained a certain amount of dicyclohexyl and a small amount of dicyclohexyldichlorosilane, which hydrolyzed in water to the dihydroxy derivative. Dicyclohexyldihydroxysilane was unstable, giving a mixture of condensation products from which $[(C_6H_{11})_2SiO]_7$ was identified. Kipping also believed he had identified varying amounts of polymeric dicyclohexyldihydroxysilane and of 1,2,2-tricyclohexyl-1,1,2-trihydroxydisilane.

Returning to the sodium reactions, the forty-third paper[46] reviewed the preparation of tetraphenylsilane and triphenylsilane. The formation of the latter was not due to the action of sodium hydride, as was demonstrated by testing the action of this reagent on phenyltrichlorosilane. There was no reaction. The work was continued, however[47].

In 1932 Kipping and Evison[48] explored the practicability of using aluminum chloride in silicon syntheses. Aluminum chloride dissolved in diphenyldichlorosilane at room temperatures but no HCl was evolved below 100°. With ethyl bromide, the reaction commenced, $SiCl_4$, $C_6H_5SiCl_3$ and various ethylated benzenes being formed. The following mechanism for the simpler reactions was proposed:

$$(C_6H_5)_2SiCl_2 + AlCl_3 \rightarrow C_6H_5AlCl_2 + C_6H_5SiCl_3$$
$$C_6H_5SiCl_3 + AlCl_3 \rightarrow C_6H_5AlCl_2 + SiCl_4$$
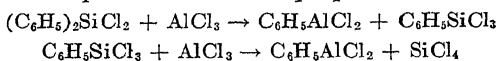
At 70° the reaction between diphenyldichlorosilane and aluminum chloride formed tetrachlorosilane, accounting for 80 per cent of all the silicon used.

Octaphenyltetrasilane reacted with aluminum chloride in chloroform to give an insoluble product whose low hydrogen value (with piperidine) indicated that not many Si-Si bonds remained, in other words that many Si-Si bonds had been broken in the reaction.   Hexaphenylcyclotrisiloxane and tetrabenzylsilane also reacted with aluminum chloride to form tetrachlorosilane.

Evison and Kipping[57] in working up the process reported by Kipping and Murray[40] discovered small percentages of tribenzylsilane as an impurity in tetrabenzylsilane.   A bit of this second product was obtained pure, by fractional crystallization of the light petroleum ether extract from the interaction of sodium and dibenzyldichlorosilane.   The reactions here reported can best be summarized by the following equations:

$$(C_6H_5CH_2)_3SiNa + HOH \rightarrow NaOH + (C_6H_5CH_2)_3SiH$$

$$2(C_6H_5CH_2)_3SiH + O \rightarrow H_2 + ((C_6H_5CH_2)_3Si)_2O$$
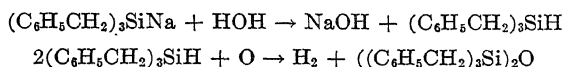
The second reaction took place in the presence of KOH in acetone.

An entirely new note in the series was struck in 1932 by Kipping and Blackburn[49] when tetraphenylsilane was nitrated in nitric acid of 1.5 density at the freezing point of water.   The products, a mixture of various tetranitrophenylsilanes totaling 93 per cent in yield, produced only 10 per cent of only one pure compound, namely, the tetra-*m*-nitrophenylsilane. This product was stable toward aluminum chloride; boiling sodium hydroxide converted it to nitrobenzene and a silicate.   Bromine formed *m*-bromonitrobenzene in 27 per cent yield.

In the same year, the next paper in the numbered series (No. 47) presented data and reactions covering additional cyclohexyl derivatives of silicon[50]:
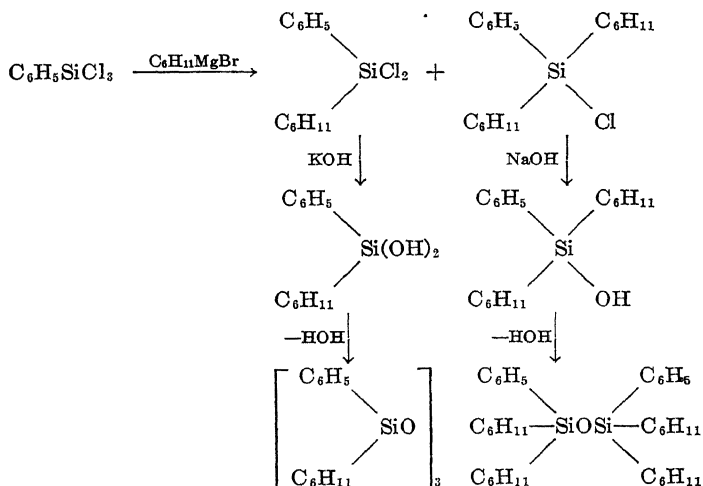
A by-product from the synthesis of cyclohexylphenyldihydroxysilane was dicyclohexyldihydroxysilane. In the following year the same authors continued their work[51] obtaining by the first Grignard reagent an 85 to 90 per cent yield of dicyclohexylcyclohexoxyphenylsilane.

Dicyclohexylphenylhydroxysilane was formed by the oxidation of dicyclohexylphenylsilane, which in turn had been prepared by the action of a cyclohexyl Grignard reagent on phenyltrichlorosilane in an atmosphere of nitrogen. Dicyclohexylphenylsilane was capable of bromination to dicyclohexylphenylbromosilane, which then reacted with ethylmagnesium bromide to form dicyclohexylphenylethylsilane.

Two papers of this series concerned themselves once again with nitration products[52, 53]. Tetra-*m*-nitrophenylsilane was reduced with zinc and hydrochloric acid to the corresponding amino compound. The tetraacetyl derivative of this amino compound was also synthesized. Reduction of the tetra-*m*-aminophenylsilane with tin and hydrochloric acid in acetone gave a tetra-*i*-propyl-*m*-aminophenylsilane. Nitration of triethylphenyl-silane with nitric acid in acetic anhydride at 0° resulted in 82 per cent para and 5 per cent meta products, reported by the authors as probably 83 per cent and 17 per cent respectively. Diphenyldiethylsilane was nitrated in the same manner to diethyldi-*m*-nitrophenylsilane, 30 per cent, along with about 70 per cent of the para isomer. Ethyltriphenylsilane was nitrated, giving 40 per cent para and 60 per cent meta, while tetraphenyl-silane formed 24 per cent para and 76 per cent meta.

A printed copy of his Bakerian lecture appeared over Kipping's signature[394] in 1937.

After a lapse of several years, Kipping's fifty-first numbered paper appeared with a description of a singular reaction by which a new orthoester of silicon was obtained[54]. It was desired to prepare $Cl_3SiC(C_6H_5)_2OMgCl$. Magnesium was found not to react with tetrachlorosilane even when boiled, but at room temperatures a perceptible reaction was noticed when the latter was first dissolved in ether. When this system was boiled and benzophenone added, there was obtained:

$$(C_6H_5)_2C-O \diagdown \quad \diagup O-C(C_6H_5)_2$$
$$Si$$
$$(C_6H_5)_2C-O \diagup \quad \diagdown O-C(C_6H_5)_2$$
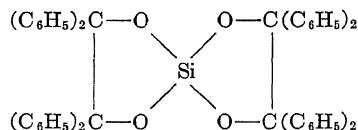
This product decomposed if held too long at its boiling point of 245°; but if it was kept at 240°, pure benzophenone distilled over.

Thus ends this resume of the contributions of Frederick S. Kipping to the organic chemistry of silicon. His original interests lay along lines of an investigation into the possibilities of the existence of optical activity in

silicon compounds analogous to those of carbon. From here he passed to the preparation of the more unusual silanes, to the formation of cyclosiloxanes and to an investigation of the existence or non-existence of doubly bound silicon. This was indeed a solid foundation on which to build.

But, contemporaneous with these papers, and weaving in and out of them so to speak in content and connotation, there is also a series of contributions from other European laboratories. These too will be considered, but in roughly chronological order, as were those of Kipping, even at the risk of a certain amount of discontinuity. To treat these papers by grouping them further as to compounds mentioned would entail considerable repetition.

Friedel and Crafts[59] in 1863 treated tetraethoxysilane with various chlorine-containing compounds, obtaining a reversal of the synthesis of the polyether:

$$3Si(OC_2H_5)_4 + SiCl_4 \rightarrow 4ClSi(OC_2H_5)_3 \qquad \text{(at 160°)}$$

PCl_3 and CH_3COCl also formed triethoxychlorosilane. Tetrachlorosilane treated with diethylzinc formed tetraethylsilane only when heated at 140° to 160° for three hours. Two years later the same workers[60, 558] applied these methods to the preparation of tetramethylsilane; they found the reaction a little more difficult, however. Dimethylmercury reacted with tetrachlorosilane with extreme difficulty. Dimethylzinc was most satisfactory at 200°. The procedure was followed at a later date by Abati[443]. In 1872, Ladenburg[66] also prepared organic compounds of silicon from polyethers:

$$2C_2H_5Si(OC_2H_5)_3 + Zn(C_2H_5)_2 + 2Na \rightarrow Zn + 2C_2H_5ONa + 2(C_2H_5)_2Si(OC_2H_5)_2$$
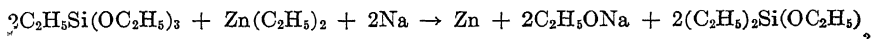
Diethylethoxychlorosilane underwent disproportionation to form a certain amount of diethyldichlorosilane which was capable of undergoing hydrolysis to hydrochloric acid and diethyloxosilane, probably polymeric.

Somewhat on a line with contemporary work by Kipping, Polis[68] presented complete experimental details for the action of sodium on a mixture of tetrachlorosilane and chlorobenzene. The organic product was tetraphenylsilane. Using *p*-bromotoluene, the product was tetra-*p*-tolylsilane. Similarly, benzyl chloride produced tetrabenzylsilane. In 1905, Taurke[86] published results of work on the conversion of chlorines in tetrachlorosilane. The section of this paper covering compounds resembling orthoesters will be discussed elsewhere, but in addition the following reactions were carried out:

$$SiCl_4 + 4iC_5H_{11}Cl + 8Na \rightarrow 8NaCl + Si(C_5H_{11}i)_4$$

$$HSiCl_3 + 3iC_5H_{11}Cl + 6Na \rightarrow 6NaCl + HSi(C_5H_{11}i)_3$$
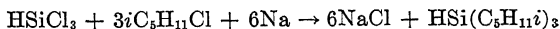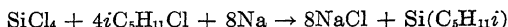
As a by-product of the second reaction was found hexa-*i*-amyldisiloxane. Tri-*i*-amylsilane was brominated giving tri-*i*-amylbromosilane, which was easily hydrolyzed in ammonia to the hydroxy derivative. Isobutyl chloride reacted as did the *i*-amyl, but more slowly, giving tri-*i*-butylsilane; this product also underwent bromination to tri-*i*-butylbromosilane.

With the intention of preparing the silicon analog of triphenylmethyl, Schlenk[80] refluxed triphenylchlorosilane in xylene with sodium under an atmosphere of nitrogen, and then filtered hot. The product was hexaphenyldisilane. It was not a free radical, as passing oxygen through its boiling solution for thirty minutes failed to have the slightest effect. Schlenk and his co-workers believed that silicon has more residual affinity than carbon. Triphenylchlorosilane was prepared by the action of acetyl chloride, then phosphorus pentachloride on triphenylhydroxysilane after the manner of Kipping[1]. Crystals of triphenylsodioxysilane or sodium triphenylsiloxide were prepared by the action of sodium on triphenylhydroxysilane in boiling toluene or xylene under nitrogen.

The German I. G. patented the preparation of tetraphenylsilane, tetrabutylsilane and tetrabenzylsilane in 1930[425]. Sodium was melted under toluene and a mixture of organic halide and tetrachlorosilane added. Later two more patents[423, 426] covered the preparation of Grignard reagents.

Mention has already been made of the use of zinc organic compounds in silicon syntheses. In 1863, Friedel and Crafts[554] found that tetrachlorosilane reacted with diethylzinc in the presence of zinc chloride to form tetraethylsilane. Chlorination of this product[555] resulted in the formation of mono and dichloro derivatives which were found to react with potassium acetate, yielding triethylacetoxyethylsilane. The acetate was then replaced by hydroxyl. Again, in 1866, Friedel and Crafts[61] reported the chlorination of tetraethylsilane. A small amount of chloroethyltriethylsilane was obtained along with an even smaller amount of higher-boiling chlorinated compounds. The fraction boiling between 180° and 200° was treated with potassium acetate as above. A small amount of hexaethyldisiloxane was obtained on final hydrolysis. Hydrolysis of ethyltrichlorosilane[65] yielded ethyloxohydroxysilane, in appearance very much like pure silica. Friedel and Ladenburg[64] carried out certain studies on the action of diethylzinc on hexachlorodisiloxane, obtaining two sets of products:

$$Cl_3SiOSiCl_3 + 3Zn(C_2H_5)_2 \rightarrow 3ZnCl_2 + (C_2H_5)_3SiOSi(C_2H_5)_3$$

$$Cl_3SiOSiCl_3 + 4Zn(C_2H_5)_2 \rightarrow 3ZnCl_2 + ZnO + 2Si(C_2H_5)_4$$
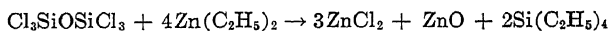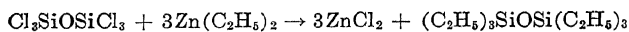
They also[413, 556, 559] treated hexaiododisilane with diethylzinc, obtaining hexaethyldisilane with a small amount of tetraethylsilane. When the former product was exposed to air, hexaethyldisiloxane was formed. This contribution was followed by another by Friedel and Crafts[87] replete with experimental data covering several series of reactions. Tetra-

ethylsilane was prepared by the action of diethylzinc on tetrachlorosilane. No appreciable amounts of any intermediate could be identified, nor was there any evidence of disproportionation between reactants and products even on an experimental run at 240°. Tetraethylsilane reacted with sulfuric acid to produce hexaethyldisiloxane. Bromine replaced one hydrogen, and when this replacement was carried out in the presence of iodine, ethyl bromide was isolated as a by-product. Bromoethyltriethylsilane reacted with potassium hydroxide to give hexaethyldisiloxane; ethylene was one of the by-products of this reaction. Chloroethyltriethylsilane reacted with potassium acetate as in a preceding reference, giving acetoxytriethylsilane. This ester, in turn, underwent potassium hydroxide saponification to the corresponding alcohol. Fuming nitric acid, reacting with tetraethylsilane, formed diethyloxosilane, probably polymerized. Tetramethylsilane was prepared by the action of dimethylmercury on tetrachlorosilane. Impure dimethyldiethylsilane was also prepared. Ladenburg[408] also reported preparation of phenyltrichlorosilane by the action of diphenylmercury on tetrachlorosilane at 300°. Absolute alcohol on the product formed phenyltriethoxysilane.

The remainder of this contribution can best be summarized by means of a diagram:

$$(C_2H_5)_3SiOC_2H_5 \xrightarrow{(CH_3CO)_2O} CH_3COOSi(C_2H_5)_3 + CH_3COOC_2H_5$$

$$\downarrow HCl$$

$$\xrightarrow{CH_3COCl} (C_2H_5)_3SiCl + CH_3COOC_2H_5$$

$$\left. \begin{array}{l} C_2H_5SiOOH \\ C_2H_4 \quad H_2 \\ SO_2 \end{array} \right\} \xleftarrow{SO_3} (C_2H_5)_3SiOH \xrightarrow{HI} \begin{array}{l} (C_2H_5)_2SiO \\ C_2H_6 \end{array}$$

$$\downarrow NH_4OH$$

$$\Big| -HOH$$

$$\xrightarrow{Na} (C_2H_5)_3SiOSi(C_2H_5)_3$$

$$\downarrow$$

$$(C_2H_5)_3SiONa$$

$$CO2 \Big|$$

$$(C_2H_5)_3SiOCOONa$$
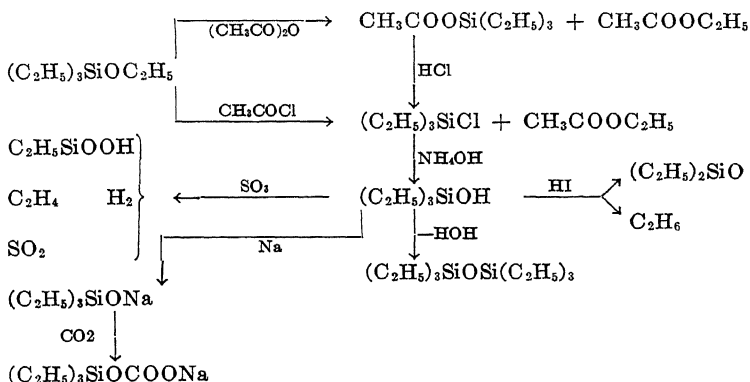
Additional data regarding the chemistry of silicon compounds which resemble orthoesters may be found elsewhere[34] and in a later chapter of this book. Conversion of ethoxytriethylsilane to a disiloxane was effected by two methods:

$$2(C_2H_5)_3SiOC_2H_5 + 2HI \rightarrow (C_2H_5)_3SiOSi(C_2H_5)_3 + 2C_2H_5I + HOH$$

$$2(C_2H_5)_3SiOC_2H_5 + 2H_2SO_4 \rightarrow (C_2H_5)_3SiOSi(C_2H_5)_3 + 2C_2H_5OSO_2OH + HOH$$
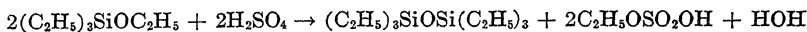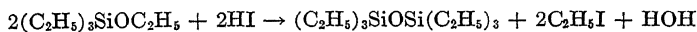
as well as by the action of P_2O_5 on triethylhydroxysilane and of potassium hydroxide on triethylchlorosilane. Tri- and tetraethylsilane were also prepared by the action of a mixture of diethylzinc and sodium on ethoxy-

triethylsilane. It may be assumed on the basis of later work that triethylsilane was formed from the tetraethylsilane by loss of ethylene. Triethylsilane passed over to hexaethyldisiloxane under the action of sulfur trioxide:

$$2(C_2H_5)_3SiH + 2SO_3 \rightarrow HOH + 2SO_2 + (C_2H_5)_3SiOSi(C_2H_5)$$
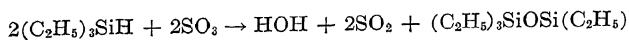
Ladenburg[67] followed with the report of work on the action of other metal organic compounds on polychlorosilanes:

$$SiCl_4 \xrightarrow{Hg(C_6H_5)_2} C_6H_5SiCl_3 + C_6H_5HgCl$$

with $C_6H_5SiCl_3$ reacting via HOH to give C_6H_5SiOOH, and via $Zn(C_2H_5)_2$ to give $C_6H_5Si(C_2H_5)_3$; the latter on heat giving $Si(C_2H_5)_4 + (C_6H_5)_2(SiC_2H_5)_2$; and $SiCl_4$ with $Zn(C_2H_5)_2$ giving $Si(C_2H_5)_4 + (C_6H_5)_2(SiC_2H_5)_2$:
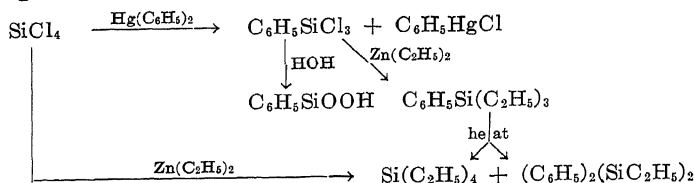
The preparation of phenyltriethylsilane was repeated[189], this time by the interaction of phenyltrichlorosilane and diethylzinc, and the principle was extended to the preparation of *p*-tolyltrichlorosilane by the interaction of tetrachlorosilane and di-*p*-tolylmercury.

In 1881, Pape[70, 347] prepared tripropylsilane and tetrapropylsilane by the action of dipropylzinc on trichlorosilane. The following equation was proposed for the reaction:

$$2HSiCl_3 + 4Zn(C_2H_5)_2 \rightarrow HSi(C_3H_7)_3 + Si(C_3H_7)_4 + 3ZnCl_2 + Zn + C_3H_8$$
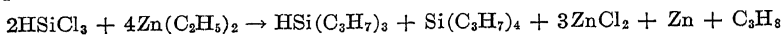
He also found that tripropylsilane could be brominated to tripropylbromosilane which was then capable of reacting with ammonia to form tripropylhydroxysilane and hexapropyldisiloxane. The bromo- compound also reacted with silver acetate to form acetoxytripropylsilane. Ladenburg continued the work[76]. Tetraphenylsilane was warmed with an equivalent amount of bromine on the water bath, then with a 10 per cent excess from 8 to 10 hours at 150° in a sealed tube. The result was the formation of bromobenzene and triphenylbromosilane. Further bromination at 150° gave diphenyldibromosilane for the preparation of which, however, Ladenburg ascribed priority to his earlier paper[67]. Triphenylbromosilane was obtained in 30 per cent yield, colorless and crystalline, and easily soluble in water, alcohol, ether or benzene. The chemistry of this compound and of some of its derivatives is shown below.

$$(C_6H_5)_3SiBr \xrightarrow{KOH\ (dil)\ (120°)} (C_6H_5)_3SiOH$$

with $(C_6H_5)_3SiBr$ reacting via $Zn(C_2H_5)_2$ to give $(C_6H_5)_3SiH$, $(C_6H_5)_3SiC_2H_5$, C_2H_4; $(C_6H_5)_3SiOH$ via H_2SO_4 giving $HOSi(C_6H_4SO_2OH)_3$ which via $BaCO_3$ gives $HOSi(C_6H_4SO_2Oba)_3$; and $(C_6H_5)_3SiOH$ via $(CH_3CO)_2O\ (140°)$ giving $CH_3COOSi(C_6H_5)_3$ which via $HONO_2$ (fuming) gives $HOSi(C_6H_3(NO_2)SO_2OH)_3$:
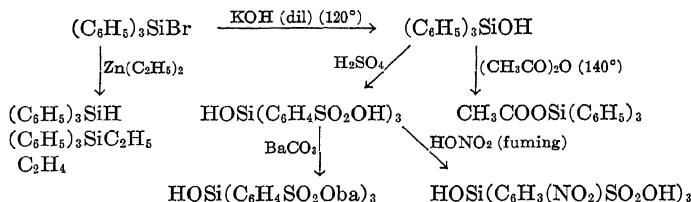
It so happened that in a previous paper Ladenburg[76] had analyzed the barium salt of triphenylhydroxysilane trisulfonic acid for carbon and hydrogen but not for silicon. Kipping pointed out soon thereafter that the figures so obtained did not differ materially from what would have been expected had the compound been the barium salt of benzene sulfonic acid. This statement may be open to question on the part of the analytical chemist of today, but at least it bore some weight at the time. Ladenburg[77] replied by publishing analytical figures for silicon as well as carbon and hydrogen, 3.3 per cent with 3.0 per cent as the calculated value.

Bygden[550] in 1917 sulfonated trimethylbenzylsilane with chlorosulfonic acid in chloroform, converting it without difficulty to the monosulfonic acid. Salts and other derivatives were also prepared, $e.g.$, $(CH_3)_3SiCH_2C_6H_4$-$SO_2ONH_3CH_3$ and its homolog with ethyl in place of methyl on the nitrogen. There were also prepared compounds with the following in place of the hydroxyl of the sulfonic acid: Cl, Br, NH_2, $NHCH_3$, $NHCH_2C_6H_5$, NHC_6H_5, $N(CH_3)C_6H_5$, $NHC_6H_4CH_3$-o, $NHC_6H_4CH_3$-p.

By far the greater number and volume of syntheses, however, have been carried out with the Grignard reagent.

Dilthey and Eduardoff[74] in 1904 prepared a series of phenylchlorosilanes by a carefully worked out set of experiments to which Kipping himself made frequent allusion. By the action of phenylmagnesium bromide on tetrachlorosilane these workers made phenyltrichlorosilane, diphenyldichlorosilane and triphenylchlorosilane. They were unable to obtain any tetraphenylsilane even after three days of cooking. Triphenylhydroxysilane and diphenyldihydroxysilane were also prepared, the latter showing a melting point of 139°. It was believed that this product was purer than Polis', since his compound melted over a range of two degrees, 139° to 141°. There were also prepared, by hydrolysis and dehydration, phenyloxohydroxysilane, diphenyloxosilane (probably polymerized) and hexaphenyldisiloxane. Dilthey alone[75] continued this work, ascertaining that the diphenyloxosilane was trimeric. The determination of its molecular weight was carried out cryoscopically in benzene. Only when benzylmagnesium chloride was used with tetrachlorosilane in the molar proportions of 4:1 was Dilthey able to obtain a satisfactory yield of tribenzylchlorosilane.

Melzer[78] prepared several organochlorosilanes by the action of the proper Grignard reagent on tetrachlorosilane, namely propyltrichlorosilane, i-amyltrichlorosilane, benzyltrichlorosilane, and α-naphthyltrichlorosilane.

Bygden[236] in 1911 reported preparation of tetramethyl- and tetraethylsilane by the action of the suitable Grignard reagent on tetrachlorosilane. Mixed alkyl-substituted silanes were also prepared by the action of methylmagnesium bromide on partially alkylated chlorosilanes; for instance, methylmagnesium bromide reacted with ethyltrichlorosilane to form

ethyltrimethylsilane. In this manner Bygden prepared propyltrimethyl-silane, diethyldimethylsilane, butyltrimethylsilane, ethylpropyldimethyl-silane, *i*-amyltrimethylsilane and *i*-butyltrimethylsilane.

In 1917, Grüttner and Krause[188] carried out very extensive work begin-ning with the preparation of *p*-halogenophenyltrichlorosilanes. Their work can best be summarized by the use of diagrammatic equations as shown below:

$$p\text{-}ClC_6H_4MgBr \xrightarrow{SiCl_4} p\text{-}ClC_6H_4SiCl_3$$

$(C_6H_5)_2AsCl$ / C_2H_5MgBr \
Na

$$(C_6H_5)_2AsC_6H_4SiCl_3 \qquad\qquad p\text{-}ClC_6H_4Si(C_2H_5)_3$$

$$p\text{-}BrC_6H_4MgBr \xrightarrow{SiCl_4} p\text{-}BrC_6H_4SiCl_3 + (p\text{-}BrC_6H_4)_2SiCl_2$$
(oil) (white prisms)

C_2H_5MgBr | \ HOH (easily)

$$p\text{-}BrC_6H_4Si(C_2H_5)_3 \qquad p\text{-}BrC_6H_4SiOOH$$

Mg |

$$p\text{-}BrMgC_6H_4Si(C_2H_5)_3 \xrightarrow{(C_2H_5)_3SnBr} (C_2H_5)_3SnC_6H_4Si(C_2H_5)_3$$

Br_2 / $(CH_3)_3PbBr$ I_2 \

$$(CH_3)_3PbC_6H_4Si(C_2H_5)_3 \qquad p\text{-}IC_6H_4Si(C_2H_5)_3$$
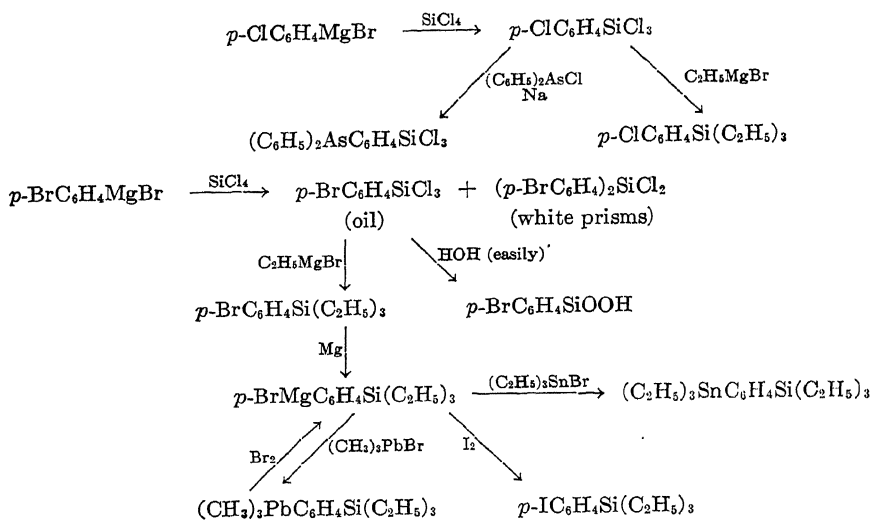
p-Chlorophenyltripropylsilane was also prepared.

Grüttner and Cauer[192] continued the work in the following year:

$$p\text{-}BrC_6H_4SiCl_3 \xrightarrow{C_2H_5MgBr} p\text{-}BrC_6H_4Si(C_2H_5)_3 \qquad (C_2H_5)_3SiOH$$

Mg /   ↑ HCl (fuming)

$$p\text{-}BrMgC_6H_4Si(C_2H_5)_3$$

$$\xrightarrow{CH_3CHO} \xrightarrow{HOH} p\text{-}CH_3CH(OH)C_6H_4Si(C_2H_5)_3$$

$$\xrightarrow{C_2H_5CHO} \xrightarrow{HOH} p\text{-}C_2H_5CH(OH)C_6H_4Si(C_2H_5)_3$$

$$\xrightarrow{C_3H_7CHO} \xrightarrow{HOH} p\text{-}C_3H_7CH(OH)C_6H_4Si(C_2H_5)_3$$

$$\xrightarrow{iC_3H_7CHO} \xrightarrow{HOH} p\text{-}i\text{-}C_3H_7CH(OH)C_6H_4Si(C_2H_5)_3$$

$$\xrightarrow{SiCl_4} p\text{-}Cl_3SiC_6H_4Si(C_2H_5)_3$$
(penetrating odor, easily hydrolized)

C_2H_5MgBr |

$$p\text{-}(C_2H_5)_3SiC_6H_4Si(C_2H_5)_3$$

$p\text{-}C_6H_4Br_2$ \
+   ← $\xrightarrow{Br_2(Fe)}$ /
$(C_2H_5)_3SiBr$ / (very slowly)
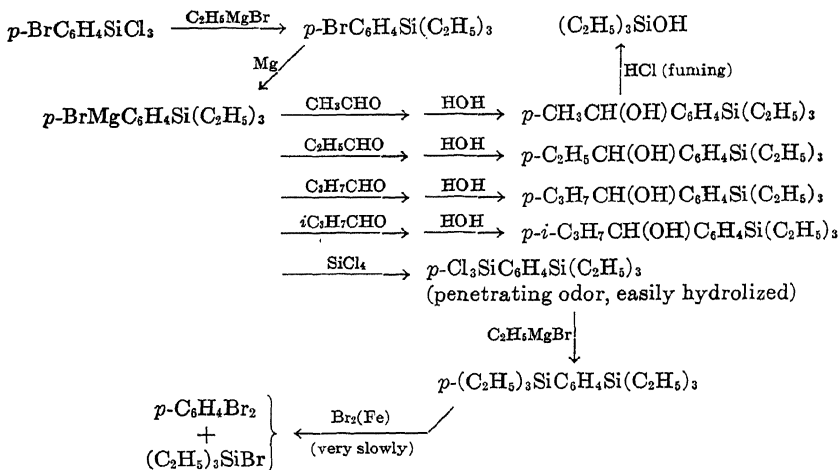
The preparation of p-iodophenyltriethylsilane by the method of Grüttner and Krause was later duplicated by Arthur Bygden[419]. Alkyl groups were introduced as follows:

$$
\begin{matrix}
\left.\begin{array}{l} C_6H_5SiCl_3 \\ p\text{-}C_6H_4Br_2 \\ Mg \end{array}\right\} \rightarrow &
\begin{array}{c} C_6H_5 \\ \diagdown \\ SiCl_2 \\ \diagup \\ p\text{-}BrC_6H_4 \end{array}
\xrightarrow{C_2H_5MgBr} &
\begin{array}{c} C_6H_5 \\ \diagdown \\ Si(C_2H_5)_2 \\ \diagup \\ p\text{-}BrC_6H_4 \end{array}
\end{matrix}
$$

$$\xdownarrow{C_2H_5MgBr}$$

$$
\begin{array}{c} C_6H_5 \\ \diagdown \\ Si(C_2H_5)_2 \\ \diagup \\ p\text{-}C_2H_5C_6H_4 \end{array}
$$
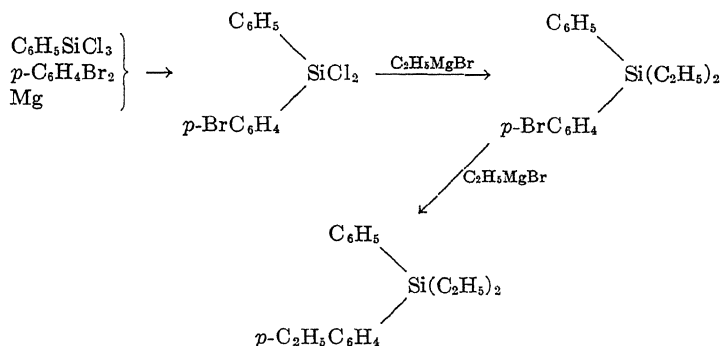
Krause and Renwanz[202] in 1929 synthesized tetra-α-thienylsilane by the interaction of α-iodothiophene, magnesium and tetrachlorosilane in absolute ether. The product was extracted with benzene.

Reynolds, Bigelow and Kraus[203] prepared triphenylsilane by the action of phenylmagnesium bromide on trichlorosilane in 73 per cent yield. Triphenylsilane reacted with metallic sodium in liquid ammonia to form di-triphenylsilicyl amine, resistant to boiling caustic. Hydrochloric acid, however, caused a splitting of this amine to triphenylhydroxysilane and ammonium chloride. Bromine was found to react quantitatively with triphenylsilane forming triphenylbromosilane and hydrobromic acid. Kraus felt that neither Ladenburg[76] nor Kipping[41] had obtained pure triphenylsilane. He disagreed with Ladenburg's melting points and stated that Kipping's inability to crystallize his product indicated a situation far from a state of complete purity.

From the laboratories of the National University of Peiping[204] comes a report of the preparation of tetraethyl and tetrabutylsilanes. The work is the more interesting because of the fact that the workers started literally from the earth itself. Sand was treated with magnesium to make silicon, which was then allowed to react with chlorine forming tetrachlorosilane. Ethylmagnesium bromide acting on tetrachlorosilane gave tetraethylsilane in 45.5 per cent yield and the corresponding reaction with butylmagnesium bromide gave the butyl compound in 44.5 per cent yield.

Medoks and Kotelkov[211] described the action of phenylmagnesium bromide on tetrafluorosilane at room temperatures. Even when an excess of the former reagent was used, no more than three radicals were introduced in place of fluorines. Triphenylfluorosilane resisted the hydrolyzing action of water. In 1938, Medoks[214] presented a method for preparing tri-

benzylfluorosilane by the interaction at room temperatures of benzyl-magnesium chloride and tetrafluorosilane. Only a little tetrabenzylsilane was formed during this reaction. Soshestvenskaya[215] in the same year prepared tetrabenzylsilane by the interaction of sodium fluorosilicate and benzylmagnesium chloride in 20.7 per cent yield; full details are listed in *Chemical Abstracts*. The author later commented[225] that it was found more advantageous to use five times the theoretical amount of sodium fluoro-silicate, by which modification it was possible to increase the yield of tetrabenzylsilane to 53.5 per cent. Monelkin and Yakubova[226] presented improvements in technique designed in general to increase the yields of tetrabenzyl and other tetra-substituted silanes still more.

In 1919, Stock and Somieski[98] prepared chlorosilane by the action of silane on hydrochloric acid in the presence of aluminum chloride. Di-chlorosilane was also formed to the extent of 20 per cent of the total yield. A detailed listing of the physical and chemical properties of chlorosilane was given in the original paper. When treated with dimethylzinc, chloro-silane formed methylsilane:

$$2H_3SiCl + Zn(CH_3)_2 \rightarrow ZnCl_2 + 2CH_3SiH_3$$
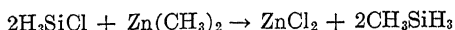
Methylsilane also reacted with 30 per cent sodium hydroxide:

$$HOH + CH_3SiH_3 + NaOH \rightarrow 3H_2 + CH_3SiOONa$$

The latter product immediately polymerized. Methylsilane, treated with hydrochloric acid under aluminum chloride catalysis, formed methyl-chlorosilane and methyldichlorosilane. These also proved quite reactive:

$$2CH_3SiH_2Cl + Zn(CH_3)_2 \rightarrow ZnCl_2 + 2(CH_3)_2SiH_2$$
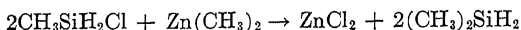
A Russian patent exists[316] covering the absorption of acetylene, ethylene and their homologs, and even of carbon monoxide, by tetrachlorosilane. Effective catalysts are one or more inert gases together with aluminum oxychloride or some other metallic halide.

Calingaert and associates[219] have determined the amount of radical interchange between tetra-substituted silanes. Thus tetraethylsilane and tetrapropylsilane reacted to give

$$5\% \ Si(C_2H_5)_4$$
$$21\% \ C_3H_7Si(C_2H_5)_3$$
$$40\% \ (C_3H_7)_2Si(C_2H_5)_2$$
$$24\% \ C_2H_5Si(C_3H_7)_3$$
$$10\% \ Si(C_3H_7)_4$$
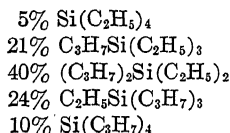
Polis nitrated tetraphenylsilane[71] very carefully with fuming nitric acid and concentrated sulfuric acid at zero degrees obtaining a mixture of

mononitro- derivatives, melting from 93° to 105°. Not even by starting with a definite isomeric chloro- compound could he obtain definite results. Nitration of tetra-*p*-tolylsilane produced silica and dinitrotoluene. Phosphorus pentachloride acting on tetraphenylsilane formed triphenylchlorosilane, diphenyldichlorosilane, chlorobenzene and phosphorus trichloride. Other investigators[577] in 1925 isolated pure *p*-nitrobromobenzene after brominating tetra-*p*-nitrophenylsilane with excess bromine from 30 to 40 hours at 100°.

Relative rates of bromination of triethylfluorosilane, triethylchlorosilane and triethylbromosilane have been studied[176]. Temperatures of 100° and 108° were used, with ethylene dibromide as the solvent.

Ushakov and Itenberg[212] have reported the chlorination of tetraethylsilane using 1 to 2 per cent of phosphorus pentachloride as catalyst; a 75 per cent yield of triethyl-α-chloroethylsilane, triethyl-β-chloroethylsilane and other chloro- derivatives was obtained. The alpha derivative lost chlorine easily with alcoholic caustic, while the beta required a temperature of 145° Each gave an isolable organic product, in each case triethylvinylsilane. This compound, strangely enough, did not polymerize even when benzoyl peroxide or sulfuric acid was used as a catalyst.

In 1912, Geoffrey Martin[237] presented certain very fundamental concepts with regard to the evolution of hydrogen gas from an organic polysilane on treatment with caustic alkali or similar agent. By the action of ethylmagnesium bromide on tetrachlorosilane and by certain well-timed items of procedure in working up the products, Martin prepared a compound of the composition 16.5 per cent C, 4.5 per cent H and 40.1 per cent Si. This would indicate, according to Martin, a formula $(C_2H_5)_2Si_4O_7H_6$ with three Si—Si linkages. The theoretical composition of this compound is 16.5 per cent C, 5.5 per cent H and 39.2 per cent Si.

After being heated for several weeks at 160°, this product was found to have lost its ability to generate hydrogen. Then on raising the temperature to 400° to 500° hydrogen came off in amounts approximately the equivalent of what would have evolved at lower temperatures with potassium hydroxide. Heating with dilute hydrochloric acid or acetic acid had the same effect as heating at 160° for a long period of time. Martin suggested the scheme on page 40.

The alpha-naphthyl compound, $C_{10}H_7Si_6O_{12}H_5$, was prepared, as was the ethyl, and was found to have the same general properties with regard to the evolution of hydrogen. It will be noted that while the ratio of silicon to ethyl was 2, the ratio of silicon to naphthyl was 6. In other corresponding products the ratio of silicon to phenyl was 4 and of silicon to benzyl 8/3.

$$SiOOH$$
$$|$$
$$C_2H_5SiOH$$
$$|$$
$$Si(OH)_2$$
$$|$$
$$C_2H_5Si(OH)_2$$

$$\xrightarrow{6KOH}$$

$$SiOOK$$
$$|$$
$$O$$
$$|$$
$$C_2H_5SiOK$$
$$|$$
$$O$$
$$|$$
$$Si(OK)_2$$
$$|$$
$$O$$
$$|$$
$$C_2H_5Si(OK)_2$$
$$+$$
$$3H_2$$

$$\xrightarrow{6HCl}$$

$$SiOOH$$
$$|$$
$$O$$
$$|$$
$$C_2H_5SiOH$$
$$|$$
$$O$$
$$|$$
$$SiO$$
$$|$$
$$O$$
$$|$$
$$C_2H_5SiO$$

htg with HCl or CH₃COOH

htg at 400°–500°

$$C_2H_5Si \begin{array}{c} SiO \\ \diagup \quad \diagdown \\ O \qquad O \end{array} + \; 3H_2$$

$$SiOOH$$
$$|$$
$$O$$
$$|$$
$$C_2H_5SiH$$
$$|$$
$$O$$
$$|$$
$$HSiOH$$
$$|$$
$$O$$
$$|$$
$$C_2H_5SiOH$$

$$\xrightarrow[400°-500°]{htg \; at}$$

$$+ \; 3H_2$$
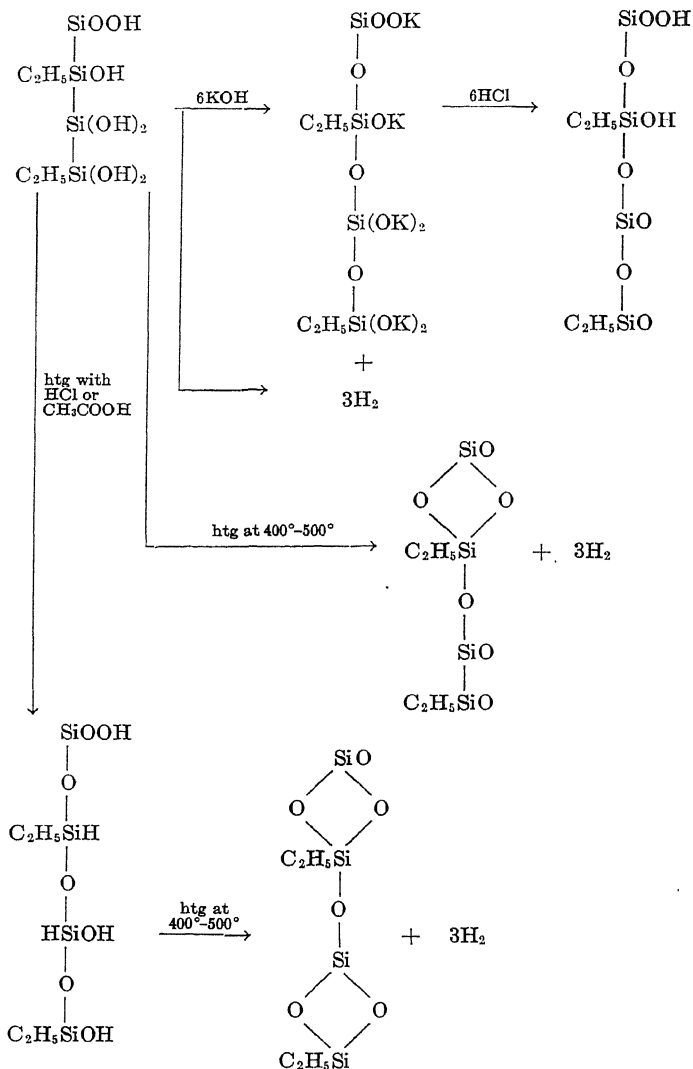
Stock[530] reported extensive evolution of hydrogen as the result of the action of caustic on methylsilane:

$$xCH_3SiH_3 + 2xHOH(NaOH) \rightarrow (CH_3SiOOH)_x + 3xH_2$$

$$x(CH_3)_2SiH_2 + xHOH(NaOH) \rightarrow ((CH_3)_2SiO)_x + 2xH_2$$
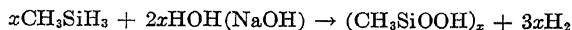
and then in excess alkali:

$$[(CH_3)_2SiO]_x + 2xNaOH \rightarrow xHOH + x(CH_3)_2Si(ONa)_2$$
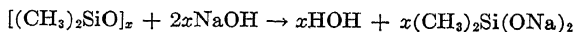
Martin reported a study on the dimorphism of dibenzyldihydroxysilane[81] and in 1913[97, 350] he carried out a reaction between methylmagnesium iodide and hexachlorodisilane which gave a yellow powder, insoluble in acids and organic solvents. Potassium hydroxide, however, caused evolution of hydrogen, thus providing evidence of Si-Si linkages. Martin believed that at least 70 per cent of the Si-Si linkages were broken by the action of the Grignard reagent, giving rise to methyltrichlorosilane, dimethyldichlorosilane and trimethylchlorosilane. The yellow precipitate had the formula $CH_3Si_6O_{13}H_9$. Hydrogen was evolved, as stated, with potassium hydroxide at the rate of 169 cc per gram of silicon treated. Martin therefore wrote its formula as

$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-O-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-\underset{}{\overset{\overset{O}{\|}}{Si}}-O-\underset{\underset{OH}{|}}{\overset{\overset{OH}{|}}{Si}}-\underset{}{\overset{\overset{O}{\|}}{Si}}-OH$$
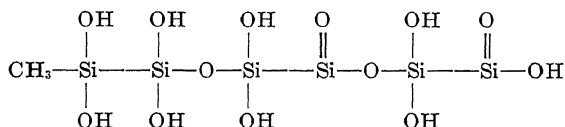
When this product was heated between 200° and 400° it lost methane and hydrogen, giving a compound free of carbon but still retaining its Si-Si linkages, as shown by its tendency to evolve hydrogen gas with potassium hydroxide. When the final potassium hydroxide solution was acidified, silica precipitated. Martin[566] continued the work on oxygen compounds, opening his paper with a reply to a statement by Kipping[17] which was rather critical of a previous contribution of Martin's[81]. Kipping's statement had cast some doubt on the identity of Martin's diphenyldihydroxysilane.

Attention has already been called to Stock's[98] reaction between methylsilane and alkalies:

$$HOH + CH_3SiH_3 + NaOH \rightarrow 3H_2 + CH_3SiOONa$$

The sodium salt immediately polymerized.

Schlenk[82] announced, in 1912, the preparation of a compound with a double bond between silicon and carbon. It was reported that diphenylmethylcarbinol lost water on crystallization to form 1,1-diphenylethylene; hence the corresponding silicon compound should be expected to do the same. Consequently, diphenyldichlorosilane was prepared and caused to react with methylmagnesium iodide to form diphenylmethylchlorosilane. This compound hydrolyzed to the corresponding hydroxy derivative which, however, could not be isolated. On the contrary diphenylmethylenesilane or $(C_6H_5)_2Si=CH_2$ was found on distillation, according to Schlenk.

Ipatiev and Dolgov[181, 418] heated tetraethylsilane with hydrogen under pressure and at 350°, obtaining ethane and triethylsilane. Phenyltriethylsilane formed benzene:

$$Si(C_2H_5)_4 + H_2 \rightarrow C_2H_6 + (C_2H_5)_3SiH$$
$$C_6H_5Si(C_2H_5)_3 + H_2 \rightarrow C_6H_6 + (C_2H_5)_3SiH$$
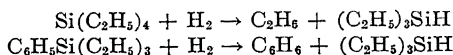
Tetraphenylsilane was found to be stable at 490°, above which temperature it condensed to give substances of high molecular weight.

In 1931, Dolgov and Vol'nov[177, 415] published further conclusions on the tendencies of tetra-substituted silanes to undergo disproportionation. Tetrabenzylsilane underwent no reaction whatsoever when heated over 400° with hydrogen at 100 atmospheres. The authors believed that the silicon inhibited any action, since tetraphenylmethane easily reacts under these conditions, splitting off benzene. There is also the matter of the relative atomic volumes to be considered: silicon is so much larger than carbon. Again, there is a difference in the behavior of the corresponding hydroxyl derivatives, as triphenylcarbinol easily reduces to triphenylmethane while triphenylhydroxysilane simply dehydrates to the ether analog. Referring to Ladenburg's[189] statement to the effect that in some cases disproportionation and radical interchange took place between trisubstituted silanes, Dolgov and Vol'nov reported that triphenylchlorosilane, when treated with diethylzinc at 230° gave, in addition to the normal product triphenylethylsilane, measurable amounts of diethyldiphenylsilane and of tetraethylsilane. Under pressure, 60 per cent of the material disproportionated. Also, hydrogenation of phenyltriethylsilane yielded benzene and hexaethyldisilane:

$$2C_6H_5Si(C_2H_5)_3 + H_2 \rightarrow 2C_6H_6 + (C_2H_5)_3SiSi(C_2H_5)_3$$
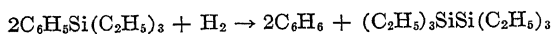
Thus a series of silanes was selected, of the type $RSiR'_3$ and heated from 24 to 48 hours each, at 300°, in hydrogen at 100 atmospheres each; these were phenyltrimethylsilane, ethyltrimethylsilane, ethyltriphenylsilane, propyltriethylsilane, i-butyltriethylsilane and i-amyltriethylsilane. In each case there was rearrangement and reaction according to the scheme:

$$2RSiR'_3 \rightarrow R_2SiR'_2 + R'_4Si$$
$$H_2 + 2RSiR'_3 \rightarrow 2RH + R'_3SiSiR'_3$$
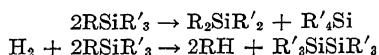
The authors' conclusions were that only when there were radicals attached to silicon as in $RSiR'_3$, that is, three of one kind and one of another, would rearrangement and decomposition with hydrogen take place readily. One phenyl group moved rather easily, but two on the same silicon seemed to stabilize each other. It was always the radical which had no counterpart within the molecule which moved. Incidentally, their attempts to prepare a urethane ended in an entirely unexpected type of reaction:

$$2(C_6H_5)_3SiOH + 2C_6H_5NCO \rightarrow (C_6H_5)_3SiOSi(C_6H_5)_3 + CO_2 + (C_6H_5NH)_2CO$$
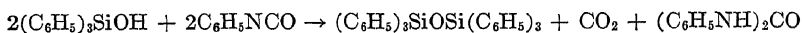
and the reaction with phenol resulted in the formation of hexaphenyldisilane, under similar conditions of hydrogenation.

In 1937, Helm and Mack[206] reported that the thermal decomposition of tetramethylsilane at temperatures between 659° and 717° was homogeneous and unimolecular at pressures above 100 mm. The decomposition

took on a higher order of reaction at low pressures, however, giving carbon, silicon, and gases.

Phenyltrihydroxysilane, benzyltrihydroxysilane, and naphthyltrihydroxysilane were prepared by Koton[220] by hydrolyzing the proper chlorine derivatives. Diphenyldipropylsilane was found to give glass-like polymers. The chlorides were made by dropping a Grignard solution on tetrachlorosilane in absolute ether.

Attempts have been made from time to time to prepare compounds, heterocyclic in nature, with rings consisting only of carbons and silicons. In 1889, W. B. Hart[319] treated tetrachlorosilane and 1,3-dibromopropane with sodium, forming trimethylenedichlorosilane:

$$SiCl_4 + CH_2(CH_2Br)_2 + 4Na \longrightarrow 2NaCl + 2NaBr + \text{(ring)}$$
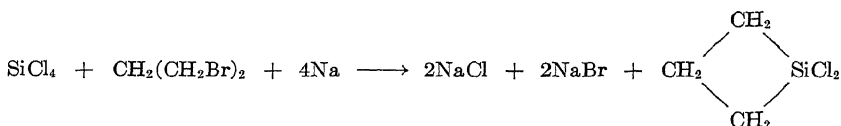
The product was not isolable in an absolutely pure state. It hydrolyzed, however, to hydrochloric acid and the corresponding silicone in moist air. A second compound was also prepared in rather impure state:

$$2 \text{ (ring with Cl, Cl)} + SiCl_4 + 8Na \longrightarrow 8NaCl + \text{(product)}$$
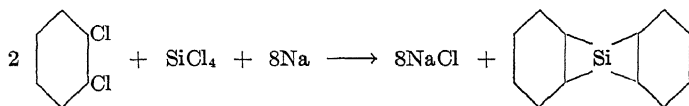
R. R. Widdowson[416] raised strong objections to Hart's work. On repeating the procedures, he was unable to isolate any products at all; consequently he stated over his signature that the record of these compounds could very well be omitted from the literature.

Grüttner and Wiernik[407] laid claim to priority in the preparation of pentamethylenediethylsilane, although their yields were admittedly very low. Bygden[318], with the idea of improving on Hart's methods, prepared the pentamethylene analog. His belief was that a six-membered ring might be more stable and therefore more easily crystallizable. This product resuled from the action of tetrachlorosilane on 1,5-amylenedimagnesium dibromide, $CH_2(CH_2CH_2MgBr)_2$, in the molar ratio of 7:5. The theoretical ratio for the formation of the desired product would have been 1:1. The yield of pentamethylene dichlorosilane amounted to 59 per cent. Certain precautions for the use of this Grignard reagent were listed in the original paper. This compound hydrolyzed to the corresponding silicone just as did Hart's product. When treated with methylmagnesium bromide the dichloro- compound formed pentamethylenedimethylsilane; viscous polymeric by-products were also listed. Pentamethylenediethylsilane was prepared by the same method.

Schwarz has reviewed[216] the methods for the preparation of chlorinated higher homologs of silane.

Stock[149] has presented a review of organic compounds of silicon to date of publication.

The study of the crystalline structures of organic compounds of silicon was begun by Polis[71] in 1886 covering tetraphenylsilane, triphenylchlorosilane, tetra-*p*-tolylsilane and tetra-*m*-tolylsilane. This has been followed, at intervals, by the work of George Jerusalem[570] and of W. H. George[560].

Wintgen[193] reported values for vapor pressures and heats of vaporization of methylsilane and dimethylsilane.

Jaeger and Dijkstra[404, 405, 406] have determined the atomic weight of silicon of terrestrial origin and have compared this value with those determined on silicon taken from certain meteorites. In the words of *Chemical Abstracts*, within the limits of "highest obtainable accuracy, terrestrial and cosmic silicon must be regarded as having the same ratio of isotopes." The silicon was converted to tetraethylsilane by the Grignard type of synthesis.

Sugden and Wilkins[409] prepared several well known silicon compounds for the purpose of determining the parachor of silicon. An average obtained from a study of $SiCl_4$, $Si(OCH_3)_4$, $Si(OC_2H_5)_4$, $Si(C_2H_5)_4$, $Si(C_3H_7)_4$ and $Si(C_6H_5)_4$ gave a value of 27.8. The two polyethers were prepared by the action of the proper anhydrous alcohol on tetrachlorosilane, and the last three compounds by the action of the appropriate Grignard reagent on the same chloride.

Discussion of the solubility of organic compounds of silicon was undertaken by Bjerrum and Josefowicz[528] in 1932; in 1933 and 1935[539, 553] it was extended to cover melting points and other physical properties.

One of the most complete lists of physical data on these compounds was published by A. Bygden[195] in 1916. Melting points, boiling points and densities were given for thirty alkyl and aryl silanes and some of their chlorine substitution products. These data will be found in Chapter 10 under their respective compound headings.

Data on the dielectric constants[536] of organic compounds of silicon appeared in 1946.

Table 2
Preparation of Organic Compounds of Silicon, Classified by Reagents
HEAT
$(C_6H_5)_3SiH$, $Si(C_6H_5)_4$ (41, 46); $(C_2H_5)_2Si_4O_6$, $(C_2H_5)_2Si_4O_7$, $(C_2H_5)_2Si_4O_7H_4$ (237)

DISPROPORTIONATION
$Si(CH_3)_4$, $(CH_3)_2Si(C_2H_5)_2$ (177); $Si(C_2H_5)_4$ (67, 177); $(C_2H_5)_3SiC_3H_7$ (215); $(C_2H_5)_2Si(C_3H_7)_2$ (177, 215); $C_2H_5Si(C_3H_7)_3$ (215); $(C_2H_5)_2Si(C_4H_9i)_2$, $(C_2H_5)_2Si(C_5H_{11}i)_2$, $(CH_3)_2Si(C_6H_5)_2$ (177); $(C_2H_5)_2Si(C_6H_5)_2$ (67, 177); $Si(C_6H_5)_4$ (177)

Table 2—*Continued*

HYDROGEN

$(C_2H_5)_3SiH$ (177); $(CH_3)_3SiSi(CH_3)_3$, $(C_2H_5)_3SiSi(C_2H_5)_3$ (177); $Si(C_6H_4NH_2-m)_4$ (52, 53); $(C_6H_5)_3SiSi(C_6H_5)_3$ (177);

SODIUM

$C_3H_6SiCl_2$ (319); $(CH_2BrCH_2)_2SiCl_2$ (319, 416); $(CH_2)_5SiCl_2$ (318); $(C_2H_5)_3SiONa$ (66); $(CH_2)_5Si(CH_3)_2$ (318); $Si(C_2H_5)_4$ (1) $(CH_2)_5Si(C_2H_5)_2$ (318, 407); $(C_4H_9)_3SiH$ (86); $(C_6H_5)_2SiCl_2$ (1); $Si(C_6H_4)_2$ (319, 416); $(iC_5H_{11})_3SiH$ (86); $Si(C_4H_9)_4$ (425); $(C_6H_5)_3SiCl$ (1); $(C_6H_5)_3SiONa$ (80); $Si(C_5H_{11}i)_4$ (86); $Si(C_6H_5)_4$, $Si(C_6H_4CH_3-p)_4$, $Si(CH_2C_6H_5)_5$ (68, 425); $C_6H_5Si(C_2H_5)Si(C_2H_5)C_6H_5$ (13); $C_6H_5Si(C_3H_7)(C_2H_5)Si(C_2H_5)(C_3H_7)C_6H_5$ (27); $(iC_5H_{11})_3SiOSi(C_5H_{11}i)_3$ (86); $(C_6H_5)_3SiSi(C_6H_5)_3$ (13, 80); $Si_4(C_6H_5)_8$ (28, 33, 36, 37); $Si_4(C_6H_4CH_3-p)_3$ (44); $OSi_4(CH_2C_6H_5)_8$ (40)

MAGNESIUM

$p-BrMgC_6H_4Si(C_2H_5)_3$ (186, 192)

OXYGEN

$C_6H_5Si(C_6H_{11})_2OH$ (51); $OSi_4(C_6H_5)_8$ (28, 44); $O_2Si_4(C_6H_5)_8$ (28)

HALOGEN

$(C_2H_5)_3SiBr$ (192); $(C_2H_5)_3SiCH_2CH_2Cl$ (61, 212); $(C_2H_5)_3SiCHClCH_3$ (212); $(C_2H_5)_3SiCH_2CH_2Br$ (87); $(C_3H_7)_3SiBr$ (70); $p-IC_6H_4Si(C_2H_5)_3$ (186, 192, 419); $(C_6H_5)_2SiBr_2$ (76); $(iC_4H_9)_3SiBr$, $(iC_5H_{11})_3SiBr$ (86); $(C_6H_5)_2Si(C_6H_{11})Br$ (51); $(C_6H_5)_3SiBr$ (76, 203); $(C_6H_5CH_2)_3SiCl$ (75); $(C_6H_5)_8Si_4I_4$ (28, 44)

WATER

C_2H_5SiOOH (65); $C_5H_{10}SiO$ (318); $C_6H_{11}SiOOH$ (45); $(C_2H_5)_3SiOH$ (66); C_6H_5SiOOH (67, 74); $p-BrC_6H_4SiOOH$ (186); $C_6H_5Si(OH)_3$, $C_6H_5CH_2Si(OH)_3$ (220); $p-CH_3C_6H_4SiOOH$ (32); $(C_2H_5)_3SiCH_2CH_2OH$ (61, 87); $C_6H_5Si(C_2H_5)O$ (3, 5, 368); $C_6H_5Si(C_2H_5)(OH)_2$ (20); $(C_3H_7)_3SiOH$ (70); $\alpha-C_{10}H_7SiOOH$ (220); $C_6H_5Si(C_3H_7)(C_2H_5)OH_7$ $C_6H_5CH_2Si(C_3H_7)(C_2H_5)OH$ (2, 3); $C_3H_7Si(C_2H_5)(OH)CH_2C_6H_4SO_2OH-p$, $(C_6H_{11})_2Si(OH)_2$ (45); $C_6H_5Si(C_6H_{11})(OH)_2$ (50); $(C_6H_5)_2SiOH)_2$ (17, 18, 29, 74); $(C_6H_5)_2Si=CH_2$ (82); $C_6H_5CH_2Si(iC_4H_9)(C_2H_5)OH$ (16); $(C_6H_5CH_2)_2Si(OH)_2$ (5); $(p-CH_3C_6H_4)_2Si(OH)_2$ (32); $(p-CH_3C_6H_4)_2SiO$ (15, 19); $(i-C_5H_{11})_3SiOH$ (86); $(C_6H_5)_3SiOH$ (74, 76, 368); $(C_6H_5CH_2)_3SiOH$ (5, 58); $(C_6H_{11}SiO)_2O$ (45); $(C_2H_5)_3SiOSi(C_2H_5)_3$ (61, 66, 87); $C_6H_5Si(C_2H_5)(OH)OSi(C_6H_5)(C_2H_5)OH$ (20); $(C_3H_7)_3SiOSi(C_3H_7)_3$ (70); $C_6H_5CH_2Si(C_2H_5)_2OSi(C_2H_5)_2CH_2C_6H_5$ (15); $C_6H_5Si(C_3H_7)(C_2H_5)OSi(C_2H_5)(C_3H_7)C_6H_5$ (2); $(C_6H_5)_2Si(OH)OSi(C_6H_5)_2OH$ (18); $C_6H_5CH_2Si(C_3H_7)(C_2H_5)OSi(C_2H_5)(C_3H_7)CH_2C_6H_5$ (2, 3); $(C_6H_5)_2Si(CH_3)OSi(C_6H_5)_2CH_3$ (35); $C_6H_5CH_2Si(iC_4H_9)(C_2H_5)OSi(C_2H_5)(iC_4H_9)CH_2C_6H_5$ (15); $(C_6H_5CH_2)_2Si(CH_3)OSi(CH_2C_6H_5)_2CH_3$ (15), $(C_6H_5CH_2)_2Si(C_2H_5)OSi(CH_2C_6H_5)_2C_2H_5$ (5, 15); $(C_6H_5)_3SiOSi(C_6H_5)_3$ (1, 368); $(p-CH_3C_6H_4)_3SiOSi(C_6H_4CH_3-p)_3$ (58); $[(C_2H_5)_2SiO]_3$ (18); $[(C_6H_5)_2SiO]_3$ (34, 37, 74, 75); $[(C_6H_5CH_2)_2SiO]_3$ (5); $(C_6H_5CH_2)_6Si_3O_4H_2$ (21); $(p-CH_3C_6H_4)_6Si_4O_5H_2$ (32); $(C_6H_5)_8Si_4(OC_2H_5)_2$ (37); $[(p-CH_3C_6H_4)_2SiO]_6$ (32); $[(C_2H_5)_2SiO]_6$ (10)

HYDROHALOGEN ACIDS

$(C_2H_5)_2SiO$ $(C_2H_5)_3SiCl$, $(C_6H_{11})_2SiO$ (66); $(C_2H_5)_3SiOSi(C_2H_5)_3$ (84); $C_6H_5Si(C_2H_5)(OH)OSi(OH)(C_2H_5)C_6H_5$ (19); $(C_2H_5)_2Si_4O_{10}H_6$ (237)

Table 2—*Continued*

CARBON DIOXIDE

$(C_2H_5)_3SiOCOONa$ (66)

NITRIC ACID

$(C_2H_5)_2SiO$ (87); $HOSi[C_6H_3(NO_2)(SO_2OH)]_3$ (76); $C_2H_5Si(C_6H_5)_2C_6H_4NO_2-m$ (52, 53); $(C_6H_5)_3SiC_6H_4NO_2-m$ (52, 53, 71, 72); $Si(C_6H_4NO_2-m)_4$ (49)

SULFURIC ACID

$C_2H_5Si(O)CH_2C_6H_4SO_2OH-p$ (5); $C_3H_7Si(C_2H_5)(OH)CH_2C_6H_4SO_2OH-p$ (3); $(C_3H_7)_2\cdot$ $Si(C_2H_5)CH_2C_6H_4SO_2OH-p$ (3); $iC_4H_9Si(C_2H_5)(C_3H_7)CH_2C_6H_4SO_2OH-p$ (9); $HOSi(C_6H_4SO_2OH)_3$ (76); $C_3H_7Si(C_2H_5)(OH)OSi(OH)C_2H_5)C_3H_7$ (27); $C_6H_5CH_2Si\cdot$ $(C_3H_7)(C_2H_5)OSi(C_2H_5)(C_3H_7)CH_2C_6H_4SO_2OH-p$ (6, 7, 8); $HOSO_2C_6H_4CH_2Si;\cdot$ $(iC_4H_9)(C_2H_5)OSi(C_2H_5)(iC_4H_9)CH_2C_6H_4SO_2OH-p$ (6, 7, 8)

CHLOROSULFONIC ACID

$(CH_3)_3SiCH_2C_6H_4SO_2OH$ (550); $(C_3H_7)_2Si(C_2H_5)CH_2C_6H_4SO_2OH-p$ (4); C_3H_7Si $(C_2H_5)\cdot(CH_2C_6H_4SO_2OH-p)_2$ (12); $C_6H_5CH_2Si(C_2H_5)(C_3H_7)CH_2C_6H_4SO_2OH-p$ (12, 14)

SULFUR TRIOXIDE

C_2H_5SiOOH, $(C_2H_5)_3SiOSi(C_2H_5)_3$ (66)
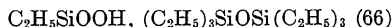
CAUSTIC ALKALIES

$CH_3SiOONa$ (98); $(C_2H_5)_3SiCH=CH_2$ (212); $(C_2H_5)_3SiOSi(C_2H_5)_3$ (87); $(C_2H_5)_2\cdot$ $Si_4O_{10}K_6$ (237)

AMMONIA

$(C_6H_5)_3SiNHSi(C_6H_5)_3$ (203)

AMINES

$C_6H_5CH_2Si(C_3H_7)(C_2H_5)NHC_6H_4CH_3-p$ (3)

SILVER ACETATE

$CH_3COOCH_2CH_2Si(C_2H_5)_3$ (61, 87); $CH_3COOSi(C_3H_7)_3$ (70)
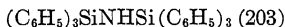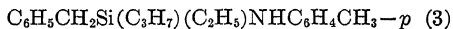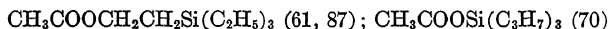
GRIGNARD REAGENTS

$C_2H_5SiCl_3$ (2, 368); $C_3H_7SiCl_3$ (74); $(CH_3)_4Si$ (236); $(C_2H_5)_2SiCl_2$ (368); $iC_5H_{11}SiCl_3$ (74); $C_5H_{10}SiCl_2$ (318); $C_2H_5Si(CH_3)_3$, $C_3H_7Si(CH_3)_3$, $(C_2H_5)_2Si(CH_3)_2$ (236); $(C_2H_5)_3$-$SiCl$ (368); $C_6H_5SiCl_3$ (17, 74, 220, 408); $C_6H_{11}SiCl_3$ (45); $p-ClC_6H_4SiCl_3$; $p-BrC_6H_4$-$SiCl_3$ (188); $iC_4H_9Si(CH_3)_3$, $C_4H_9Si(CH_3)_3$ (236); $C_5H_{10}Si(CH_3)_2$ (318); $p-CH_3C_6H_4$-$SiCl_3$ (32); $C_3H_7Si(CH_3)_2C_2H_5$ (236); $C_6H_5CH_2SiCl_3$ (78, 220); $(C_2H_5)_4Si$ (204, 236, 368, 409); $iC_5H_{11}Si(CH_3)_3$ (236); $C_6H_5Si(C_2H_5)Cl_2$ (2, 368); $C_6H_5CH_2Si(C_2H_5)Cl_2$ (3); $\alpha-C_{10}H_7SiCl_3$ (78, 220); $C_6H_5CH_2Si(C_2H_5)(CH_3)OH$, $C_6H_5CH_2Si(C_2H_5)_2OH$ (15); $C_6H_5Si(C_3H_7)(C_2H_5)Cl$ (2, 368); $C_6H_5Si(C_3H_7)(C_2H_5)CH_3$ (2); $Si(C_3H_7)_4$ (409); $(C_6H_5)_2SiCl_2$ (17, 74); $(p-BrC_6H_4)_2SiCl_2$ (186); $C_6H_5CH_2Si(C_3H_7)(C_2H_5)Cl$ (3); $C_6H_5CH_2Si(C_3H_7)(C_2H_5)OH$ (15); $C_6H_5Si(C_6H_{11})Cl_2$ (50); $p-ClC_6H_4Si(C_2H_5)_3$ (186); $p-BrC_6H_4Si(C_6H_5)Cl_2$ (192); $p-BrC_6H_4Si(C_2H_5)_3$ (186, 192); $p-(C_2H_5)_3SiC_6H_4SiCl_3$

Table 2—*Continued*

(192); $C_6H_5CH_2Si(C_3H_7)(C_2H_5)CH_3$ (3); $(C_6H_5)_2Si=CH_2$ (82); $C_6H_5CH_2(iC_4H_9)Si\cdot(C_2H_5)Cl$ (6); $(C_6H_5CH_2)_2SiCl_2$ (5); $p-ClC_6H_4Si(C_3H_7)_3$ (186, 192); $(p-CH_3C_6H_4)_2\cdot SiCl_2$ (32); $(C_6H_5CH_2)_2Si(CH_3)OH$, $(C_6H_5CH_2)_2Si(C_2H_5)OH$ (15); $(C_6H_5CH_2)_2Si\cdot(C_2H_5)Cl$ (12); $C_6H_5CH_2Si(C_4H_9)(C_3H_7)C_2H_5$ (9); $[\alpha-C_4H_3S]_4Si$ (202); $p-BrC_6H_4Si\cdot(C_2H_5)_2C_6H_5$ (192); $(C_2H_5)_3SiF$ (211); $(C_6H_5)_3SiCl$ (74); $(C_6H_5)_3SiOH$ (15); $p-C_2H_5\cdot C_6H_4Si(C_2H_5)_2C_6H_5$ (192); $C_6H_5CH_2Si(C_6H_5)(C_3H_7)C_2H_5$ (2); $(C_6H_5)_3SiH$ (203); $C_6H_5Si(C_6H_{11})_2Cl$ (50); $C_6H_5SiH(C_6H_{11})_2$ (51); $(C_6H_5CH_2)_2Si(C_3H_7)C_2H_5$ (12); $C_6H_5Si\cdot(C_6H_{11})_2C_2H_5$ (51); $(p-CH_3C_6H_4)_3SiCl$ (58); $(C_6H_5CH_2)_3SiF$ (214); $(C_6H_5CH_2)_3SiCl$ (5); $Si(C_6H_5)_4$ (409); $Si(CH_2C_6H_5)_4$ (215); $(C_6H_5)_8Si_4O$, $[(C_6H_5)_8Si_4(C_2H_5)_2](HOH)_3$ (31); $CH_3Si_6O_{13}H_9$ (97)

ZINC ALKYLS

CH_3SiH_3, $(CH_3)_2SiH_2$ (98); $Si(CH_3)_4$ (60, 87); $Si(C_2H_5)_4$ (59, 64, 67, 169, 443, 554, 557); $(C_3H_7)_3SiH$ (70); $C_6H_5Si(C_2H_5)_3$ (67, 189); $(C_6H_5)_2Si(C_2H_5)_2$ (177); $(C_6H_5)_3SiH$ (76); $C_2H_5Si(C_6H_5)_3$ (76, 177); $(C_2H_5)_3SiSi(C_2H_5)_3$ (413, 557); $(C_2H_5)_3SiOSi(C_2H_5)_3$ (64)

MERCURIC ALKYLS

$Si(CH_4)_4$ (60, 87); $C_rH_5SiCl_3$ (67); $p-CH_3C_6H_4SiCl_3$ (189)

ALUMINUM CHLORIDE

$SiCl_4$, $C_6H_5SiCl_3$ (48)

TRIETHYLSTANNIC BROMIDE

$p-(C_2H_5)_3SnC_6H_4Si(C_2H_5)_3$ (186)

TRIMETHYLLEAD BROMIDE

$p-(CH_3)_3PbC_6H_4Si(C_2H_5)_3$ (186, 192)

PHOSPHORUS PENTACHLORIDE

$(C_2H_5O)_3SiCl$ (59); $(C_6H_5)_2SiCl_2$, $(C_6H_5)_3SiCl$ (71, 72)

SODIUM + DIETHYLZINC

$(C_2H_5)_2Si(OC_2H_5)_2$ (66)

SODIUM + DIPHENYLCHLOROARSINE

$p-(C_6H_5)_2AsC_6H_4Si(C_2H_5)_3$ (186)

MAGNESIUM + BENZOPHENONE

$Si[OC(C_6H_5)_2]_4$ (154)

ACETYLENE TETRACHLORIDE

$(C_6H_5)_8Si_4O$, $(C_6H_5)_8Si_4O_2$ (30)

ALDEHYDES

$p-CH_3CH(OH)C_6H_4Si(C_2H_5)_3$, $p-C_2H_5CH(OH)C_6H_4Si(C_2H_5)_3$, $p-C_3H_7CH(OH)\cdot C_6H_4Si(C_2H_5)_3$, $p-iC_3H_7CH(OH)C_6H_4Si(C_2H_5)_3$ (192)

Table 2—*Continued*

ACID CHLORIDES

$C_6H_5CH_2Si(C_2H_5)(OH)_2$ (80); $C_6H_5CH_2Si(C_2H_5)_2Cl$ (15); $C_6H_5Si(C_6H_{11})_2OH$ (51); $(C_6H_5)_3SiCl$ (80); $CH_3COOSi(C_6H_5)_3$ (368); $(C_6H_5CH_2)_3SiCl$ (10); $(C_6H_5)_3SiOH$, $[(C_6H_5)_2SiO]_4$ (18)

PHENYL ISOCYANATE

$[(C_6H_5)_3Si]_2O$ (177)

OXYGEN

$(C_2H_5)_3SiOSi(C_2H_5)_3$ (413)

Chapter 4

Organic Compounds of Silicon Prepared at
Moderate Temperatures
(Journal Literature)

Practically at the end of this, the Kipping era, there began the period of dual production from both academic and industrial laboratories. This chapter is therefore a review of the journal literature published during the period when the patent literature on organic compounds of silicon also was growing. Because of the enormous volume of this material, the patent literature itself will be discussed in a separate chapter, immediately following this. Chapter 6 will concern itself with the syntheses of organic compounds of silicon involving much higher temperatures than those outlined in Chapters 3, 4 and 5.

Under suitable conditions, organometallic compounds will react with halogen derivatives with interchange of halogen and radical. The beginnings of this type of synthesis have already been pointed out.

In 1938, Schumb, Ackerman and Saffer[93] presented an article describing applications of the Wurtz-Fittig synthesis to the preparation of alkylchlorosilanes. In this work it was discovered that the action of sodium on a mixture of an alkyl or aryl halide and, for instance, hexachlorodisilane or hexachlorodisiloxane, brought about fission of the silicon-silicon linkage as well as of the silicon-oxygen. Both these types of compounds reacted to form only tetrasubstituted silanes. To make sure that the substituted disilanes or disiloxanes had not been ruptured at the temperatures used, or with excess sodium, hexaphenyldisilane was boiled with excess sodium for ten hours with and without chlorobenzene, but with no result. Yields are shown on page 50.

Schumb and Saffer[91] continued the work in 1941 with further reports on two-stage reactions with silicon halides. Here the "intermediate sodium compound was first prepared from chlorobenzene and sodium. Then the silicon halide was allowed to react with it." Using hexachlorodisilane and hexachlorodisiloxane, a certain amount of tetraphenylsilane was formed in each case, but the main products were hexaphenyldisilane and hexaphenyldisiloxane, respectively. It seemed to the authors that "in the

ordinary one-stage Wurtz reaction the energy liberated in the system by the formation of sodium phenyl is enough to rupture the silicon-silicon and silicon-oxygen bonds. When this energy is evolved and dissipated before the silicon halide is added, no fission occurs." This type of explanation is not without precedent in chemical reasoning, as witness Tschitschibabin's[84,] [94] explanation of the general action of Grignard reagents on orthoesters. It was also assumed that the formation of some tetraphenylsilane could be explained by postulating an incomplete reaction between chlorobenzene and sodium. Phenylsodium in excess reacted with tetrachlorosilane exactly as did the Grignard reagent. A new compound was prepared by the condensation of hexachlorodisilane with benzylsodium, namely hexabenzyl-disilane. The identity of this product was checked by its preparation by means of another method, the action of benzylmagnesium chloride on hexachlorodisilane.

Table 3.

Reactants + Na	Products	Yields (%)	Found
$SiCl_4 + p\text{-}ClC_6H_4C_6H_5$	$Si(C_6H_4C_6H_5\text{-}p)_4$	90	m.p. 274°
$SiCl_4 + C_5H_{11}Cl$	$Si(C_5H_{11})_4$	80	b.p. 318°
$Si_2Cl_6 + C_2H_5Br$	$Si(C_2H_5)_4$	low	b.p. 150°
$Si_2Cl_6 + C_5H_{11}Cl$	$Si(C_5H_{11})_4$	60	b.p. 305°–312°
$Si_2Cl_6 + C_6H_5Cl$	$Si(C_6H_5)_4$	60	m.p. 231°
$Cl_3SiOSiCl_3 + C_6H_5Cl$	$Si(C_6H_5)_4$	60	m.p. 227°
$Cl_3SiOSiCl_3 + C_2H_5Br$	$Si(C_2H_5)_4$	low	b.p. 150°–158°

Kraus and Eatough[324] treated triphenylbromosilane with lithium in the presence of ethyl amine and isolated what purported to be a free radical, triphenylsilicyl, with one equivalent of ethyl amine of crystallization. This was shown to be a stable entity, melting at 45° C. The reaction was carried out in ethyl amine solution and the molecular weight of the product was determined in benzene. Further chemistry of this compound and certain of its derivatives is indicated below.

$$
\begin{matrix}
(C_6H_5)_3SiBr \\
Li \\
C_2H_5NH_2
\end{matrix} \Big\} \longrightarrow \Big\{
\begin{matrix}
LiBr \\
[(C_6H_5)_3Si](C_2H_5NH_2)
\end{matrix}
$$

Li ↙   ↘ heat

$(C_6H_5)_3SiSn(CH_3)_3$ ←$\xrightarrow{(CH_3)_3SnCl}$— $(C_6H_5)_3SiLi$ $(C_6H_5)_3SiSi(C_6H_5)_3$

↓ Br_2 NH_4Br ↙   ↘ C_6H_5Br

$(C_6H_5)_3SiBr$ $(C_6H_5)_3SiH$ $Si(C_6H_5)_4$
$(CH_3)_3SnBr$
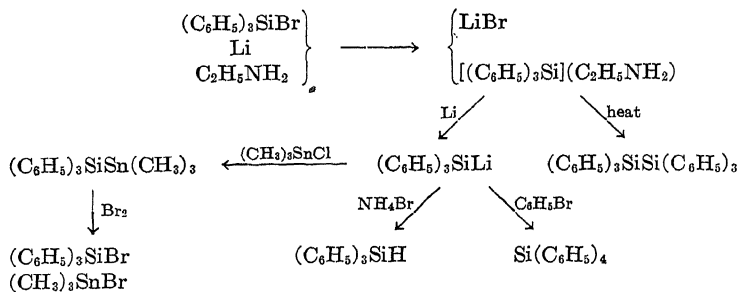
Ethyl amine is a weaker ammonolyzing agent than ammonia; hence it was not surprising that this work should have been more successful in the prep-

aration of triphenylsilicyl than was the previous attempt using ammonia. In 1946, Gilman and Massie[338] prepared triethylmethylsilane by the action of methyllithium on triethylsilane. The system was stirred at room temperatures for 13 hours, then refluxed for 12.5 hours.

R. N. Meals of General Electric[362] prepared triethylsilane by Grignard reaction, and then subjected the product to the action of butyllithium. The result was the formation of triethylbutylsilane in 58 per cent yields. Similarly, propyltriethylsilane was produced in 74.5 per cent yields and phenyltriethylsilane in 81 per cent. The overall equations were:

$$SiCu + C_2H_5Cl \ (300°) \rightarrow Cu + C_2H_5SiHCl_2$$
$$C_2H_5SiHCl_2 + 2C_2H_5MgCl \rightarrow 2MgCl_2 + (C_2H_5)_3SiH$$
$$(C_2H_5)_3SiH + LiC_4H_9 \rightarrow LiH + (C_2H_5)_3SiC_4H_9$$
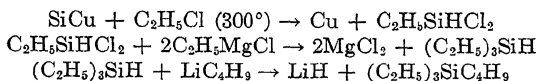
Lithium ethoxide, substituted for butyllithium, formed ethoxytriethylsilane in 74 per cent yields. These reactions might well be considered as excellent evidence for the electronegative character of hydrogen connected to silicon, a concept which was later expanded at greater length by Price[645].

Price believes that the reaction setting free hydrogen molecules from a silane can be formulated as follows:

$$(OH)^- + R_3SiH + R'OH \rightarrow R_3SiOH + (OR')^- + H_2$$
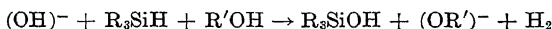
The data were characterized as indicating effects similar to carbon compounds undergoing "neucleophilic attack", *i.e.*, larger substituents definitely inhibit the action. Using triethylsilane, it was found that an almost quantitative evolution of hydrogen resulted when the silane was treated with (a) NaOH or KOH in absolute ethanol, (b) KOH in 95 per cent ethanol, (c) KOH in butanol and (d) sodium butoxide in butanol.

It was stated that "More than just a silane and hydroxide must be involved. . . ." To check the hypothesis that hydrogen anion is immediately neutralized by hydrogen cation, a series of experiments was run with water added to the ethanol. Work at two temperatures permitted calculation of energies and entropies of activation. The reaction is of the first order with respect to silane, hydroxide and probably "hydroxylated solvent." Increasing the size of the group attached to silicon or of the radical in RONa has an inhibiting effect.

Diethylmethylsilane, dipropylmethylsilane and dimethylpropylsilane were prepared for the first time.

Certain reactions from Whitmore's laboratories[582], discussed more fully later in this chapter, could also be interpreted as substantiating the concept of negative hydrogen attached to silicon:

$$(C_2H_5)_3SiH + (C_2H_5)_2SiCl_2(AlCl_3) \rightarrow (C_2H_5)_2SiH_2 + (C_2H_5)_2SiHCl + (C_2H_5)_3SiCl$$
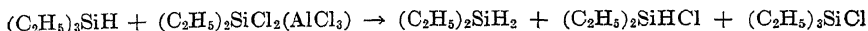
There were other reactions of the same type.

Gilman and Clark[449] have prepared several more compounds of silicon by means of organic compounds of lithium:

$$SiCl_4 + 4LiC_2H_5 \rightarrow 4LiCl + Si(C_2H_5)_4 \quad (92\% \text{ yield})$$
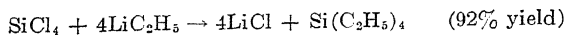
Similarly, yields of tetrabutylsilane and tetraphenylsilane were 98 and 99 per cent, respectively. Using tetraethoxysilane instead of the tetrachloro compound, a 97 per cent yield of tetrabutylsilane was obtained and a 98 per cent yield of tetraphenylsilane. Use of tetraethylmercaptosilane gave a 98 per cent yield of tetraphenylsilane.

A mixture of three equivalents of phenyllithium to one of tetrachlorosilane resulted in the formation of triphenylchlorosilane, which hydrolyzed to triphenylhydroxysilane with an overall yield of 97 per cent. The chloro compound gave a 91 per cent yield of triphenyl-p-tolylsilane when treated with p-tolyllithium. In similar fashion, diphenyl-p-tolylsilane was also prepared in 78 per cent yield.

The same authors[522] later presented interesting reactions leading to the synthesis of i-propyl derivatives of silane:
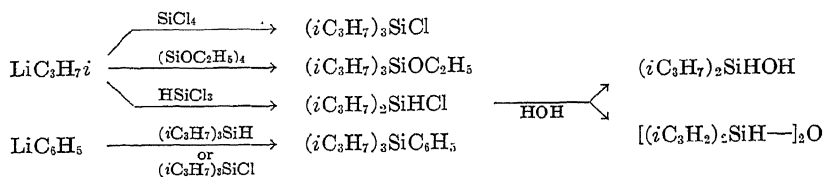
Failure to replace all of the chlorines in $SiCl_4$ or $HSiCl_3$ when the i-propyl reagent was used was ascribed to some steric effect due to the organic radical involved. o-Tolyllithium showed the same phenomenon but phenyllithium, as shown, did not.

Gilman and co-workers[562] have found that diethylbarium does not react with tetraphenylsilane.

Gilliam, Liebhafsky and Winslow[95] heated dimethylmercury with tetrachlorosilane both with and without aluminum chloride, but without satisfactory results; nor were the results any better when dimethylzinc was used in place of the mercury compound. Dry diethyl or dibutyl ether was a satisfactory solvent in both cases. Later the Grignard reagent was found to be superior:

$$CH_3MgCl + SiCl_4 \rightarrow CH_3SiCl_3 + MgCl_2$$
$$2CH_3MgCl + SiCl_4 \rightarrow (CH_3)_2SiCl_2 + 2MgCl_2$$
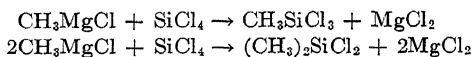
Attention was called to the anomalous fact that both of these products boil around 70°, well above the spread between the boiling points of tetramethylsilane and tetrachlorosilane.

Emeleus and Wilkins[291] have prepared fluorosilanes by the action of zinc

fluoride on the corresponding compounds; thus there were prepared ethyltrifluorosilane, phenyltrifluorosilane, diethyldifluorosilane, diphenyldifluorosilane, triethylfluorosilane and triphenylfluorosilane. Compounds with three fluorines per silicon hydrolyzed with water quite easily. Those with two fluorines per silicon hydrolyzed with difficulty, while those with only one fluorine per silicon were very resistant to the hydrolyzing action of water. By the same general method, A. E. Newkirk[432] has prepared trimethylfluorosilane, dimethyldifluorosilane and methyltrifluorosilane.

The same type of replacement can also be accomplished by the use of hydrofluoric acid. Pearlson, Brice and Simons[450] studied the action of hydrofluoric acid on compounds of the type R_xSiCl_{4-x}. These reactions were fast, even without catalytic influence. No hydrocarbons were formed, nor was tetrafluorosilane; hence the carbon-silicon bond must have lived up to its expectations with regard to stability. Anhydrous hydrofluoric acid was used in a copper vessel, ice-cooled, and the organic silicon chloride added. The system was allowed to warm to room temperature over night, the excess hydrofluoric acid removed with sodium fluoride, and the precipitate washed with benzene. Thus there were prepared $C_5H_{11}SiF_3$, $(C_5H_{11})_2SiF_2$, $(C_5H_{11})_3SiF$, $(C_6H_5)_2SiF_2$, $C_4H_9SiF_3$, $(C_4H_9)_2SiF_2$, $(C_4H_9)_3SiF$, CH_3SiF_3 and $(CH_3)_2SiF_2$. Reactivities of these compounds varied with the number of fluorines per molecule.

Booth and co-workers in 1946 presented a series of syntheses covering the substitution of fluorine for chlorine in organic compounds of silicon. The replacing agent was antimony trifluoride with or without the catalyzing influence of such compounds as antimony pentafluoride or pentachloride. Thus, with P. H. Carnell[395] ethyltrichlorosilane was synthesized by way of the Grignard reagent using one mole of the latter to five of tetrachlorosilane. The yield of ethyltrichlorosilane amounted to between 59 and 80 per cent. Treatment of this product with antimony trifluoride produced ethylfluorodichlorosilane, ethyldifluorochlorosilane and ethyltrifluorosilane. Physical constants obtained in the course of this work are listed in Chapter 10. In similar manner, with H. S. Halbedel[396] the corresponding propyl compounds were prepared and with W. F. Martin the methyls[397]. In the work with methyltrichlorosilane, antimony pentafluoride was used as a catalyst. Booth and J. F. Suttle[398] prepared and studied dimethyldifluorosilane, trimethylchlorosilane and trimethylfluorosilane. Booth and Spessard[399] and Booth and Schwartz[400] prepared all possible mixed chlorofluorosilanes containing one butyl or i-propyl radical per molecule. Antimony trifluoride was the catalyst.

In 1934, Kraus and Nelson[85] prepared triethylsilane by the interaction of an ethyl Grignard reagent and trichlorosilane, in the molar proportion of 3 to 1. In 1936, Gierut, Sowa and Nieuwland[171] published procedures

for the preparation of trialkylfluorosilanes by the action of the proper Grignard reagent on tetrafluorosilane:

$$SiF_4 + 3C_2H_5MgCl \rightarrow 3MgFCl + (C_2H_5)_3SiF$$
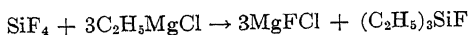
Yields were reported as 45 per cent for triethylfluorosilane, 62 per cent for the corresponding propyl compound, 70.1 per cent for the butyl, and 57.6 per cent for the amyl. Chlorides were found more adaptable than bromides or iodides in preparing and using the Grignard reagents. The products were very stable. Fluorine attached to silicon was not attacked even by sodium in liquid ammonia.

In 1939, Schumb and Saffer[88] reported preparation of only "partially substituted" silanes by interaction of the Grignard reagent with various halogen derivatives of silane, polysilanes and siloxanes. A 40 per cent yield of hexaphenyldisilane was obtained using the proper Grignard reagent and the method of Cusa and Kipping[51], whereby higher temperatures were made available:

$$6C_6H_5MgBr + Cl_3SiSiCl_3 \rightarrow 3MgBr_2 + 3MgCl_2 + (C_6H_5)_3SiSi(C_6H_5)_3$$
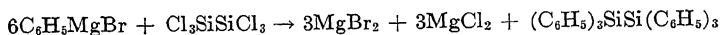
If in this work[88] diphenyldichlorosilane had been formed, as had been reported[89] for a Grignard reaction in the "usual" manner, then most assuredly some tetraphenylsilane would also have been formed "of which we were unable to isolate more than a minute amount. In other experiments it was found possible to identify as little as 1 per cent of tetraphenylsilane in a mixture with hexaphenyldisilane." Thus Schumb and Saffer asserted their conviction that the silicon-silicon bond was not broken under the conditions of their experiments. Certainly their results bore out this statement.

Hexachlorodisilane reacted with *p*-tolylmagnesium bromide forming hexa-*p*-tolyldisilane in 30 per cent yield. Hexabromodisilane reacted with phenylmagnesium bromide, however, to give tetraphenylsilane and only a small amount of the disilane. Tetrabromosilane reacted with phenylmagnesium bromide at 175 to 190° to give a 60 per cent yield of tetraphenylsilane. These results were comparable to those of Cusa and Kipping[51]. Schumb and Saffer reported the addition of magnesium to a mixture of tetrachlorosilane and bromobenzene to proceed quite smoothly. The reaction was vigorous, but the overall time was thereby shortened by two hours.

As for the effect of position isomerism, it should be noted here that tetrachlorosilane did not react with *o*-tolylmagnesium bromide, whereas the meta isomer gave a yield of 8 per cent and the para 35 per cent.

Octachlorotrisilane reacted with phenylmagnesium bromide to form only tetraphenylsilane and hexaphenyldisilane. A 40 per cent yield of

hexaphenyldisiloxane resulted when hexachlorodisiloxane reacted with phenylmagnesium bromide. Hexabromodisiloxane gave some of the desired product, but also some triphenylhydroxysilane. Octabromo-trisiloxane formed only triphenylhydroxysilane. Thus it is quite evident that the silicon-chlorine bond can be more often relied upon to do as it is expected to do than the silicon-bromine linkage, at least under the influence of the high temperatures involved here.

Ethylmagnesium bromide reacted with hexachlorodisilane giving a 50 per cent yield of hexaethyldisilane together with a very little tetra-ethylsilane. Propylmagnesium chloride followed the same pattern in its reaction.

In the original article, physical data were presented regarding Si_2Cl_6, Si_2Br_6, Si_2OCl_6, Si_2OBr_6, $Si_3O_2Br_8$, $Si(C_2H_5)_4$, $Si(C_3H_7)_4$, $(C_6H_5)_3SiOH$, $Si(C_6H_5)_4$, $Si(C_6H_4CH_3-m)_4$, $Si(C_6H_4CH_3-p)_4$, $(C_2H_5)_3SiSi(C_2H_5)_3$, $(C_3H_7)_3SiSi(C_3H_7)_3$, $(C_6H_5)_3SiSi(C_6H_5)_3$, $(p-CH_3C_6H_4)_3SiSi(C_6H_4CH_3-p)_3$, $(C_6H_5)_3SiOSi(C_6H_5)_3$. These data may also be found appropriately listed in Chapter 10. Vol'nov and Reutt[224] prepared hexaacetylenyldisiloxane in yields of between 3 and 5 per cent. The first stage was the action of tet-rachlorosilane on acetylenylmagnesium bromide. The reaction was violent. The system was allowed to stand over night, then warmed for three hours, water added, the ether boiled off and the product recrystal-lized from alcohol. R. M. Fuoss has contributed[548] some theoretical con-siderations concerning the interaction of the Grignard reagent and tetra-chlorosilane.

Trichlorosilane, made from hydrochloric acid and ferrosilicon[230], will react with methylmagnesium bromide to give a good yield of trimethyl-silane. This product, chlorinated at $-20°$, formed trimethylchlorosilane with a 75 per cent yield. Gilliam and Sauer[315] have reported directions for the preparation of trimethylchlorosilane by the action of methyl-magnesium chloride on a mixture of dimethyldichlorosilane and methyl-trichlorosilane.

Sauer[309] found that trimethylhydroxysilane dehydrated more easily than its higher homologs; in fact this tendency seriously hampered its isolation. Dehydration could be hastened by potassium carbonate or activated alumina. In addition, trimethylhydroxysilane formed an azeotropic mixture with the corresponding ether, hexamethyldisiloxane, boiling at $90°$. The method of Kipping and Hackford was used here:

$$[(CH_3)_2SiO]_x + xCH_3MgI \rightarrow x(CH_3)_3SiOMgI$$
$$(CH_3)_3SiOMgI + HOH \rightarrow (CH_3)_3SiOH + Mg(OH)I$$
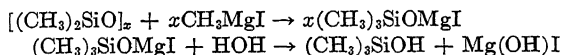
W. R. Collings[112] has described the commercial preparation of silicones through the action of the Grignard reagent at the Dow Corning plant at

Midland, Mich., and as a corollary thereto, a private communication from Dow Corning[115] listed to an exhaustive degree the physical properties of methyltrichlorosilane, dimethyldichlorosilane, ethyltrichlorosilane and diethyldichlorosilane. A copy of these data is included at this point.

Dimethyldichlorosilane $(CH_3)_2SiCl_2$, Mol. Wt. 129.0

Volatile, colorless to straw-colored liquid which fumes strongly in the air. It is decomposed by water, alcohols and ammonia. It is soluble in anhydrous hydrocarbons, ether, or chlorinated hydrocarbons. Vapors allowed to contact moist surfaces hydrolyze to form hydrochloric acid and a water-repellent film of liquid dimethyl silicone.

Caution:

Dimethyldichlorosilane is toxic, inflammable and corrosive. Breathing the vapors or contact with mucous membrane or the skin should be avoided. This material behaves in many respects like a strong acid. It should be handled with care and stored in a cool place out of contact with water.

Properties of $(CH_3)_2SiCl_2$	Physical Data on Pure Compound	Specifications of Technical Grade
Boiling Range at 740 mm.	69.4°C	68 to 71°C
Specific Gravity at 25/25°C	1.074	1.069 to 1.075
Flash Point	−9°C	−9°C
Fire Point	−9°C	−9°C
Content of $(CH_3)_2SiCl_2$	>99%	>95%
Color	Faint yellow to colorless	Straw yellow to brown

Vapor Pressure Data on Pure $(Ch_3)_2SiCl_2$

Temperature (°C)	Pressure (mm. Hg)	Temperature (°C)	Pressure (mm. Hg)
0	48	30	185
10	78	50	395
20	122	70.5	760

Methyltrichlorosilane CH_3SiCl_3, Mol. Wt. 149.5

Volatile, colorless to straw-colored liquid which fumes strongly in the air. It is decomposed by water, alcohols and ammonia. It is soluble in anhydrous hydrocarbons, ether and chlorinated hydrocarbons. Vapors allowed to contact moist surfaces hydrolyze to form hydrochloric acid and a water-repellent film of methyl silicone resin.

Caution:

Methyltrichlorosilane is toxic, inflammable and corrosive. Breathing the vapors and contact with the skin or mucous membranes should be strictly avoided. This material behaves in many respects like a strong acid and should be handled with great care and stored in a cool place out of contact with moisture.

Properties of CH₃SiCl₃	Physical Data on Pure Compound	Specifications of Technical Grade
Boiling Range at 740 mm.	64.6°C	64 to 67°C
Specific Gravity at 25/25°C	1.273	1.268 to 1.275
Flash Point	8.3	8.3
Fire Point	8.3	8.3
Content of CH₃SiCl₃	>99.8%	>95%
Color	Faint yellow to colorless	Straw

Vapor Pressure Data on Pure CH₃SiCl₃

Temperature (°C)	Pressure (mm. Hg)	Temperature (°C)	Pressure (mm. Hg)
0	54	30	212
10	89	50	450
20	140	66.5	760

Ethyltrichlorosilane $C_2H_5SiCl_3$, Mol. Wt. 163.5

Volatile, water-white to faint yellow colored liquid which fumes in the air. Decomposed by water and alcohols, soluble in anhydrous hydrocarbons, ether and chlorinated hydrocarbons. Vapors allowed to contact moist surfaces hydrolyze to form HCl and a water-repellant film of silicone resin.

Caution:

Ethyltrichlorosilane is toxic, inflammable and corrosive. Breathing the vapors and contact with the skin should be avoided. This material behaves in many respects like a strong acid. It should be handled with great care and stored out of contact with water.

Properties of C₂H₅SiCl₃	Physical Data Pure Compound	Specifications of Technical Grade
Boiling Range at 740 mm.	99 to 101°C	94 to 100°C
Specific Gravity at 25/25°C	1.242	1.238 to 1.245
Flash Point	14°C	12 to 14°C
Fire Point	14°C	12 to 14°C
Content of C₂H₅SiCl₃, not less than	99.5%	95%
Color	Faint yellow to colorless	Light straw

Vapor Pressure Data on Pure C₂H₅SiCl₃

Temperature (°C)	Pressure (mm. Hg)	Temperature (°C)	Pressure (mm. Hg)
0	8	30	44
10	14.8	50	120
20	26	99.5	760

Diethyldichlorosilane $(C_2H_5)_2SiCl_2$, Mol. Wt. 157.0

Mobile, faint yellow colored liquid which fumes in the air.   Decomposed by water and alcohols, soluble in anhydrous hydrocarbons, ether, or chlorinated hydrocarbons.   Vapors allowed to contact moist surfaces hydrolyze to form HCl and a water-repellant film of liquid silicone.

Caution:

Diethyldichlorosilane is toxic, inflammable and corrosive.   Breathing the vapors and contact with the skin should be avoided.   This material behaves in many respects like a strong acid.   It should be handled with care and stored out of contact with water.

Properties of $(C_2H_5)_2SiCl_2$	Physical Data on Pure Compound	Specifications of Technical Grade
Boiling Range at 740	130 to 131°C	124 to 130°C
Specific Gravity at 25/25°C	1.053	1.050 to 1.057
Flash Point	25°C	24 to 26°C
Fire Point	25°C	24 to 26°C
Content of $(C_2H_5)_2SiCl_2$, not less than	99.5%	95%
Color	Faint yellow to colorless	Light straw

Vapor Pressure Data on Pure $(C_2H_5)_2SiCl_2$

Temperature (°C)	Pressure (mm. Hg)	Temperature (°C)	Pressure (mm. Hg)
0	2	30	13
10	4	100	290
20	7.4	130.5	760

Burkhard[421] has prepared *p*-chlorophenyltrimethylsilane and *p*-bromophenyltrimethylsilane by the interaction of the appropriate Grignard reagent and trimethylchlorosilane:

$$(CH_3)_3SiCl + p-BrC_6H_4MgBr \rightarrow MgClBr + (CH_3)_3SiC_6H_4Br-p$$
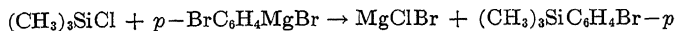
The yield was 53 per cent for the bromo compound and 83 per cent for the chloro.

From the Soviet Union has come a method[422] for the preparation of tetraethylsilane by the interaction of ethylmagnesium bromide and sodium fluorosilicate.

R. N. Lewis[446] has shown that halogen interchange between Grignard reagent and substituted silane is a factor to be reckoned with.   Ethylmagnesium bromide (18.35 moles) reacted with 24 moles of dimethyldichlorosilane to form 8.33 moles of dimethylethylchlorosilane, 0.723 mole of dimethyldiethylsilane and 1.508 moles of dimethylethylbromosilane.   Phenyldichlorosilane was prepared by the action of phenylmagnesium bromide on trichlorosilane.

Emeleus and Robinson[649] have prepared ethyldichlorosilane and diethyl-chlorosilane by the action of ethylmagnesium bromide on trichlorosilane. Other compounds similarly prepared were methyldichlorosilane, phenyl-dichlorosilane, diphenylchlorosilane, benzyldichlorosilane and dibenzyl-chlorosilane. The action of dry sodium ethoxide or methoxide on various silicon chlorides gave good yields of ethyltriethoxysilane, diethyldiethoxy-silane, ethyltrimethoxysilane and diethyldimethoxysilane.

Quite recently a series of papers has come from the laboratories of Pennsylvania State College on the subject of the alkyl silanes and their chemistry, particularly their chlorination. The first of these, by Sommers, Pietrusza, Kerr and Whitmore[453] comprises the following reactions:

$$(C_2H_5)_3SiOSi(C_2H_5)_3 + H_2SO_4 + 2NH_4Cl \rightarrow (NH_4)_2SO_4 + HOH + 2(C_2H_5)_3SiCl$$
$$(C_2H_5)_3SiOSi(C_2H_5)_3 + H_2SO_4 \rightarrow HOH + [(C_2H_5)_3Si]_2SO_4$$
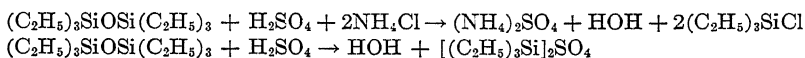
The first reaction was also satisfactory when ammonium fluoride was used; the second required fuming sulfuric acid.

Table 4.

$C_5H_{11}SiCl_3$	52%
$C_6H_{13}SiCl_3$	50%
$C_8H_{17}SiCl_3$	46%
$C_{10}H_{21}SiCl_3$	54%
$C_{12}H_{25}SiCl_3$	29%
$C_{14}H_{29}SiCl_3$	48%

The second of these[258], by Whitmore and eight associates, described the preparation of a long list of alkyl trichlorosilanes and tetraalkylsilanes, the latter for the most part having more than one kind of alkyl group per molecule. Thus hexylmagnesium bromide was allowed to react with tetrachlorosilane in the molar proportion of 3 to 2. The yields of hexyl-trichlorosilane and of other compounds similarly prepared are given in Table 4. Tetraalkylsilanes were prepared by two reactions:

$$RSiCl_3 + 3CH_3MgBr \rightarrow 3MgClBr + RSi(CH_3)_3 \qquad (A)$$
$$(CH_3)_3SiCl + RMgBr \rightarrow MgClBr + RSi(CH_3)_3 \qquad (B)$$
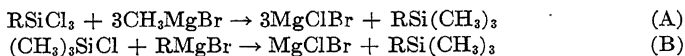
Of the two, the latter was preferred since it was the more economical of the rarer "R". Silanes prepared by these methods are given below, to-gether with the yields and the method (see above equations) by which they were prepared. Later, Whitmore and Sommer[259] chlorinated tetra-methylsilane. The silicon compound was dissolved in carbon tetra-chloride, a catalytic amount of phosphorus pentachloride added, and chlorine gas passed in for four hours at the rate of 0.5 mole per hour. During chlorination the system was exposed to radiation from a 450-watt sun-light lamp. About two-thirds of the yield consisted of polychlorinated

compounds, but the remaining third was chloromethyltrimethylsilane. Various interesting reactions were carried out with this product. It readily formed the Grignard reagent, which in turn was found to react with mercuric chloride to form the corresponding organomercuric chloride. Sodium iodide converted chloromethyltrimethylsilane to iodomethyltrimethylsilane.

Table 5.

$(CH_3)_3SiC_2H_5$	32%	A	$(C_2H_5)_3SiCH_3$	60%	B
$(CH_3)_3SiC_3H_7$	54%	A	$(C_2H_5)_3SiC_2H_5$	68%	
$(CH_3)_3SiC_4H_9$	64%	A	$(C_2H_5)_3SiC_3H_7$	71%	A
$(CH_3)_3SiC_5H_{11}$	50%	A	$(C_2H_5)_3SiC_4H_9$	50%	B
$(CH_3)_3SiC_6H_{13}$	79%	A	$(C_2H_5)_3SiC_5H_{11}$	75%	B
$(CH_3)_3SiC_7H_{15}$	46%	B	$(C_2H_5)_3SiC_6H_{13}$	60%	B
$(CH_3)_3SiC_8H_{17}$	89%	A	$(C_2H_5)_3SiC_7H_{15}$	68%	B
$(CH_3)_3SiC_{10}H_{21}$	80%	A	$(C_2H_5)_3SiC_8H_{17}$	77%	A
$(CH_3)_3SiC_{12}H_{25}$	56%	B	$(C_2H_5)_3SiC_{10}H_{21}$	78%	A
$(CH_3)_3SiC_{14}H_{29}$	50%	A			

Chloromercuriomethyltrimethylsilane, treated with methylmagnesium chloride and then with hydrochloric acid, formed methylmercuric chloride, from which result Whitmore and Sommer argued that $(CH_3)_3SiCH_2$ is more strongly electronegative than CH_3,

$$(CH_3)_3SiCH_2HgCH_3 + HCl \rightarrow (CH_3)_4Si + CH_3HgCl$$
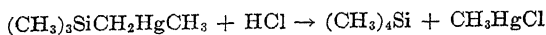
After this reaction was repeated with hexylmagnesium chloride and phenylmagnesium chloride, the following series of relative electronegativities was drawn up:

Table 6.

$$C_6H_5 > (CH_3)_3SiCH_2 > CH_3 > C_6H_{13} > (CH_3)_3CCH_2$$

The position of the silicon radical in this series was attributed to the strong electronic unsaturation of the silicon atom.

Mention was made of the "silicon effect," *i.e.*, the effect of a silicon atom on the reactivity of a functional group in an attached carbon chain. Thus much of the reactivity of $(CH_3)_3SiCH_2Cl$, as contrasted with the lethargy shown by $(CH_3)_3CCH_2Cl$, was ascribed to the size of the silicon atom as compared with carbon. Their covalent radii were given as 1.17Å and 0.77Å, respectively. The three methyl groups are spaced farther apart when they are attached to silicon, as contrasted with the situation when they are attached to carbon; therefore they do not shield as completely the carbon which is attached to chlorine. Silicon was regarded as less saturated electronically than carbon, and therefore was more capable of acting as an electron "sink."

A fourth paper by these authors[260] described further chlorinations, this time with sulfuryl chloride and benzoyl peroxide. Methyltrichlorosilane

and phenyltrichlorosilane did not chlorinate, and ethyltrichlorosilane required the catalytic action of benzoyl peroxide. With this catalyst the last-named compound formed α-chloroethyltrichlorosilane and β-chloroethyltrichlorosilane in approximately the ratio of 1 to 2.5. It is interesting to note that the two could easily be distinguished by their reactions with methyl alcoholic sodium hydroxide. The former lost only chlorine attached to silicon but the latter lost all its chlorine. Benzyltrichlorosilane also chlorinated in this manner.

α-Chloroethyltrichlorosilane reacted with methylmagnesium bromide to give a 53 per cent yield of α-chloroethyltrimethylsilane. This compound also formed the mercuric derivative, as did chloromethyltrimethylsilane.

Sommer, Dorfman, Goldberg and Whitmore[261] chlorinated propyltrichlorosilane in the same manner. The products were α-, β- and γ-chloropropyltrichlorosilanes in the ratio of 1 to 3.5 to 3.1. The chemistry of these compounds paralleled roughly those described above. Continuance of this work[271] furnished an interesting example of the fission of the carbon-silicon bond. β-Chloroethyltrichlorosilane was found to react with aqueous sodium hydroxide to form ethylene, and the corresponding propyl compound gave propylene:

$$CH_2ClCH_2SiCl_3 + 4NaOH(aq) \rightarrow C_2H_4 + Si(ONa)_4 + 4NaCl + 4HOH$$
$$CH_3CHClCH_2SiCl_3 + 4NaOH(aq) \rightarrow C_3H_6 + Si(ONa)_4 + 4NaCl + 4HOH$$
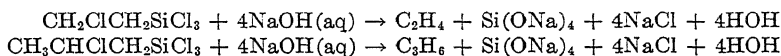
This was considered to be a case of beta elimination, not hydrolysis. Furthermore, it was known that Grignard reagents split the compound at the carbon-silicon bond:

$$CH_2ClCH_2SiCl_3 + 4CH_3MgBr \rightarrow C_2H_4 + Si(CH_3)_4 + 2MgCl_2 + 2MgBr_2$$
$$CH_2ClCH_2SiCl_3 + 4C_2H_5MgBr \rightarrow C_2H_4 + Si(C_2H_5)_4 + 2MgCl_2 + 2MgBr_2$$
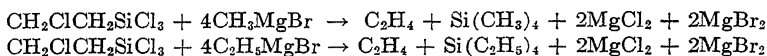
With water, alone or in ether solution, normal hydrolysis of the chlorines attached to silicon occurred, followed by immediate polymerization to the polymer represented by the formula $(CH_2ClCH_2SiO_{1.5})_x$. Sodium hydroxide hydrolysis of this polymer produced ethylene, sodium silicate and sodium chloride. It was suggested that the unique splitting of the carbon-silicon bond might have taken place as follows:
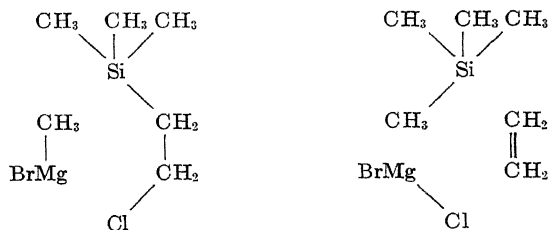
Di Giorgio, Sommer and Whitmore[314] have prepared and isolated diethyldihydroxysilane by the hydrolysis of diethyldichlorosilane. The

best hydrolyzing agents were dilute alkali, saturated sodium bicarbonate solution and concentrated sodium chloride solution.

The next paper in this series[361] described the action of ethylmagnesium bromide on tetraethoxysilane. Ethoxytriethylsilane thus formed was hydrolyzed and dehydrated in acid medium to hexaethyldisiloxane. This product was then treated with sulfuric acid and ammonium chloride to form triethylchlorosilane.

This was followed by another contribution[363] referring once more to the so-called "silicon effect." Again, triethylchlorosilane was prepared by the action of sulfuric acid and ammonium chloride on hexaethyldisiloxane, and in similar manner triethylfluorosilane was prepared using ammonium fluoride. These two compounds were chlorinated with sulfuryl chloride and benzoyl peroxide. There were prepared, in this manner, $CH_3CHClSi(C_2H_5)_2Cl$, $CH_2ClCH_2Si(C_2H_5)_2Cl$, $CH_3CHClSi(C_2H_5)_2F$ and $CH_2ClCH_2 \cdot Si(C^2H^5)2F$. In addition, α-chloroethyldiethylmethylsilane was prepared by the action of methylmagnesium bromide on the first compound listed above. In alkali titrations of these halogen derivatives, all alpha chlorines were left intact, but beta chlorines were hydrolyzed to the extent of 98 per cent. Thus $CH_3CHClSi(C_2H_5)_2OH$ was prepared in good yields. There was good evidence for the electronegativity of "neosilicon" groups, since "inertness of primary alpha C-Cl bonds in silico-neopentyl chloride toward silver nitrate is paralleled by that of secondary C-Cl bonds alpha to silicon." In fact, secondary C-Cl bonds alpha to silicon are even less reactive to silver nitrate, etc., than primary C-Cl bonds in ordinary alkyl halides.

α-Chloroethyldiethylphenylsilane was prepared by the action of phenylmagnesium bromide on the proper chlorosilane.

Whitmore and other associates[438] carried out rather extensive studies in the chemistry of monohydroxysilanes. The work reported in this paper can best be summarized by a series of diagrammatic equations.

$$(C_2H_5)_3SiOSi(C_2H_5)_3 \xrightarrow[\text{(0° to 20°)}]{H_2SO_4 \text{ (fuming)}} [(C_2H_5)_3SiO]_2SO_2$$

$$\searrow HOH$$

$$(C_2H_5)_3SiCl \xrightarrow{NaOH} (C_2H_5)_3SiOH$$

$$CH_3MgBr \Big\downarrow \qquad (CH_3CO)_2O \Big| \qquad \searrow Na$$

$$(C_2H_5)_3SiCH_3 \qquad CH_3COOSi(C_2H_5)_3 \qquad (C_2H_5)_3SiONa$$

$$(CH_3)_3SiOSi(CH_3)_3 \xrightarrow{H_2SO_4 + NH_4F} (CH_3)_3SiF$$

$$HOH + \Big\uparrow (H) + \qquad \Big\downarrow HOH$$

$$(CH_3)_3SiONa \xleftarrow{NaOH} (CH_3)_3SiOH$$
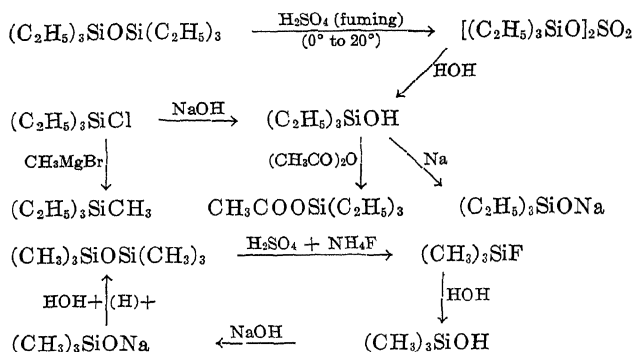
Whitmore and others[505] prepared a Grignard reagent by the action of magnesium on trimethylchloromethylsilane, then allowed this compound to react with trimethylchlorosilane and with dimethyldichlorosilane. The action of trimethylchlorosilane caused the formation of hexamethyldisilylmethylene, while dimethyldichlorosilane gave octamethyltrisilylmethylene:

$(CH_3)_3SiCH_2MgCl + (CH_3)_3SiCl \rightarrow MgCl_2 + (CH_3)_3SiCH_2Si(CH_3)_3$

$2(CH_3)_3SiCH_2MgCl + (CH_3)_2SiCl_2 \rightarrow 2MgCl_2 + (CH_3)_3SiCH_2Si(CH_3)_2CH_2Si(CH_3)_3$
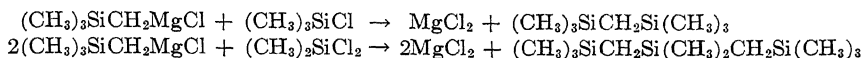
Yields ranged between 63 and 65 per cent. In addition, dimethylchloromethylchlorosilane reacted to form pentamethylchloromethyldisilylmethylene:

$(CH_3)_3SiCH_2MgCl + ClCH_2Si(CH_3)_2Cl \rightarrow MgCl_2 + ClCH_2Si(CH_3)_2CH_2Si(CH_3)_3$
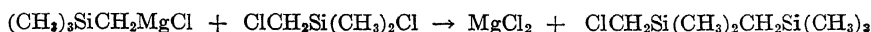
Tyler, Sommer and Whitmore[506] prepared *t*-butyltrichlorosilane by the action of *t*-butyllithium on tetrachlorosilane; then by the action of methylmagnesium bromide, they converted this product to *t*-butyltrimethylsilane. Whitmore, Pietrusza and Sommer[582] reported interaction of certain silanes and alkyl chlorides in the presence of aluminum chloride:

$(C_2H_5)_3SiH + C_6H_{13}Cl(AlCl_3) \rightarrow C_6H_{14} + (C_2H_5)_3SiCl$

$(C_2H_5)_3SiH + tC_4H_9CH_2Cl(AlCl_3) \rightarrow iC_5H_{12} + (C_2H_5)_3SiCl$

$(C_2H_5)_3SiH + tC_4H_9CH_2CH_2Cl(AlCl_3) \rightarrow (CH_3)_2CHCH(CH_3)_2 + (C_2H_5)_3SiCl$
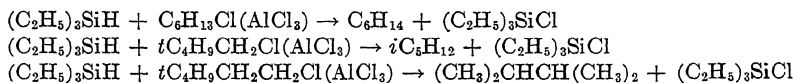
These reactions were very exothermic, and show, in the conclusions of the writers, that silicon is less negative than carbon in these compounds. It was suggested that aluminum chloride might have drawn chloride anion from carbon and that the latter might then have drawn hydrogen anion from silicon. Silicon cation could then have taken chloride anion from the complex $(AlCl_4)^-$. It was also found that hydrogen-halogen interchange also could be effected, but without appreciable heat effect:

$(C_2H_5)3SiH + (C_2H_5)_2SiCl_2(AlCl_3) \rightarrow (C_2H_5)_2SiH_2 + (C_2H_5)_2SiHCl + (C_2H_5)_3SiCl$
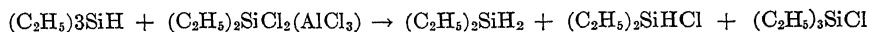
Whitmore, Sommer and Gold[660] have found that aluminum chloride, acting catalytically, converts trimethylchloromethylsilane to dimethylethylchlorosilane. The product reacted with methylmagnesium chloride to form trimethylethylsilane. As a side reaction, aluminum chloride catalyzed disproportionation of dimethylethylchlorosilane to a mixture of trimethylchlorosilane, diethylmethylchlorosilane and triethylchlorosilane. Trimethylchloromethylsilane reacted with sodium iodide to form trimethyliodomethylsilane. These reactions were discussed fully from a polar point of view.

Pietrusza, Sommer and Whitmore[654] discussed further certain phases of the action of monoalkyl substitution products of ethylene with trichloro-

silane in the presence of benzoyl peroxide and ultraviolet light. Lower yields were obtained with branched chain olefins, the peroxide proving to be a better catalyst than ultraviolet light. There were no secondary reactions in an excess of olefin using propyldichlorosilane. There was no reaction with triethoxysilane, triethylsilane or tetrachlorosilane. A free radical mechanism was favored.

Sommer, Kerr and Whitmore[650] allowed methylmagnesium bromide and ethylmagnesium bromide to compete for a given, insufficient amount of triethylchlorosilane. It was found that the silicon chloride reacted exclusively with the methyl Grignard. The action of ethylmagnesium bromide on a mixture of triethylchlorosilane and trimethylchlorosilane produced trimethylethylsilane and tetraethylsilane. Using propylmagnesium bromide, all of the product was trimethylpropylsilane.

Whitmore[581] and other associates have prepared trimethyl-β-hydroxypropylsilane by the action of $(CH_3)_3SiCH_2MgCl$ on acetaldehyde.

Whitmore[653] reported work on the action of an ammonium fluoride-sulfuric acid mixture on hexamethyldisiloxane to form trimethylfluorosilane. Similarly, trimethylchlorosilane was formed. Bromine reacted with phenyltriethylsilane to form triethylbromosilane. Iodine reacted in the same manner. Hexamethyldisiloxane was made by the action of methylmagnesium bromide on tetraethoxysilane followed by sulfuric acid hydrolysis.

Flood[410] has prepared triethylfluorosilane, triethylchlorosilane and triethylbromosilane by the action of the proper hydrohalogen acid on hexaethyldisiloxane. The hydrohalogen acid was generated *in situ* by the action of concentrated sulfuric acid on the proper sodium or ammonium salt. Patnode and Schmidt[452] have prepared a silicyl sulfate:

$$H_2SO_4 + 2(CH_3)_3SiCl \rightarrow 2HCl + [(CH_3)_3Si]_2SO_4$$
$$PbO + 2(CH_3)_3SiOH \rightarrow HOH + [(CH_3)_3SiO]_2Pb$$
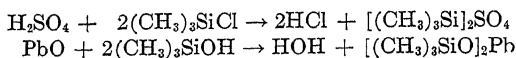
Gilman and Clark[504] treated ethyl acetoacetate with triethylchlorosilane, obtaining a derivative of the enol form which was then subjected to several metathetical reactions:

$$CH_3C(ONa)=CHCOOC_2H_5 + (C_2H_5)_3SiCl \rightarrow NaCl$$
$$+ CH_3C[OSi(C_2H_5)_3]=CHCOOC_2H_5$$
$$CH_3C[OSi(C_2H_5)_3]=CHCOOC_2H_5 + CH_3COCl \rightarrow (C_2H_5)_3SiCl$$
$$+ CH_3C(OOCCH_3)=CHCOOC_2H_5$$
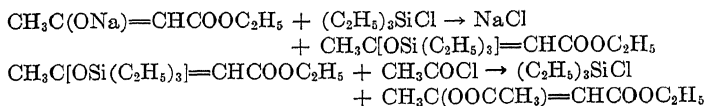
Ketonic hydrolysis of the silicon derivative of ethyl acetoacetate formed acetone and hexaethyldisiloxane. This paper has been commented on by Whitmore and co-workers[581].

Niedzielski[221] chlorinated tetraethylsilane and then treated the resulting triethyl-β-chloroethylsilane with potassium acetate and acetic acid. Thus

there was obtained triethyl-β-acetoxyethylsilane, which was quite easily saponified by potassium hydroxide in alcohol to the corresponding hydroxy derivative in 48 per cent yield:

$$Si(C_2H_5)_4 + Cl_2 \rightarrow HCl + (C_2H_5)_3SiCH_2CH_2Cl$$
$$CH_3COOK + (C_2H_5)_3SiCH_2CH_2Cl \rightarrow KCl + CH_3COOCH_2CH_2Si(C_2H_5)_3$$
$$CH_3COOCH_2CH_2Si(C_2H_5)_3 + KOH \rightarrow CH_3COOK + (C_2H_5)_3SiCH_2CH_2OH$$
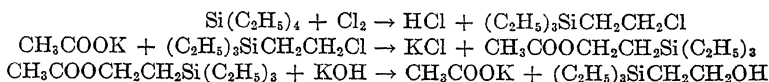
Krieble and Elliott[451] have reported the following:

$$(CH_3)_3SiCl + Cl_2 \rightarrow$$

$(CH_3)_3SiCl$ (recovered)	18.9%
$(CH_3)_2Si(CH_2Cl)Cl$	15.4%
$(CH_3)_2Si(CHCl_2)Cl$	20.7%
$CH_3Si(CH_2Cl)_2Cl$	7.65%
Residue	7.35%

$$(CH_3)_2Si(CHCl_2)Cl + NaOH(40\%) \rightarrow CH_2Cl_2$$
$$CH_3Si(CH_2Cl)Cl + KOH \rightarrow CH_3Cl$$
$$(CH_3)_3SiCl + (CH_3)_2Si(CH_2Cl)Cl \text{ (then hydrolyzed)} \rightarrow (CH_3)_3SiOSi(CH_3)_3$$
$$\rightarrow (CH_3)_3SiOSi(CH_3)_2CH_2Cl$$

$$\left[\begin{array}{c} CH_3 \\ \diagdown \\ CH_3Si \\ \diagup \\ ClCH_2 \end{array} \right] O_2$$

$$(CH_3)_2SiCl_2 + Cl_2 \rightarrow$$

$(CH_3)_2SiCl_2$ (recovered)	25.9%
$CH_3Si(CH_2Cl)Cl_2$	25.7%
$CH_3Si(CHCl_2)Cl_2$	32.5%
$CH_3Si(CCl_3)Cl_2$	6.4%

Chlorinations were carried out with the aid of a General Electric 4W "germicidal" lamp at 24° to 25°. Chlorine was passed into slightly more than a kilogram of material until 10.3 moles had been absorbed. Chloromethyl compounds with less than three chlorines on any one carbon were found to be less stable toward carbon-silicon fission by acid hydrolysis. With alkalies, as shown above, even CH_2Cl came off as CH_3Cl.

The preparation of polymeric methyloxosilanes was reported by Rochow and Gilliam[92] in 1941. Because these polymeric products resembled silica and the inorganic silicates, they were here spoken of as organo-silicon oxides. The authors referred to Kipping as first suggesting the polymeric nature of dehydrated dihydroxysilanes[2, 5, 10, 16, 19,] as well as the trihydroxysilanes[24, 26]. Ladenburg also noted some of these preparations[66, 67]. The scheme in use by Rochow and Gilliam involved hydrolysis of methyltrichlorosilane and dimethyldichlorosilane. Isolation of the pure halides mentioned did not prove practicable, but it was soon discovered that the mixtures could be hydrolyzed advantageously without isolation. For example, when such a mixture was poured over ice, hydrolysis and dehydration took place almost simultaneously with formation of chains of alternate silicon and oxygen, with oxygen cross-linkages and methyls attached to

silicon. Preliminary liquid products could eventually be condensed to solids of a resinous nature. Later, products prepared from successfully isolated methyltrichlorosilane and dimethyldichlorosilane were shown to be identical with those prepared from the mixture mentioned above. Absolute ether was the solvent. Thus, with an average of 1.0 to 1.3 as the CH_3 to Si ratio, there was produced at room temperatures a sticky, syrupy product changing to a hard transparent resin and finally passing over on warming to a brittle mass, glassy in character.

With a CH_3 to Si ratio varying between 1.3 and 1.5, condensation at room temperatures gave a colorless, oily liquid which, on being heated to 100°, increased in viscosity and lost in volatility until at temperatures between 150° and 200° it gelled, and then hardened to a transparent resin. Continued heating made the product brittle. With an average CH_3 to Si ratio of between 1.5 and 1.9 the products were volatile. If the product was heated at 200° for several hours, a soft rubbery gel was formed, which later became brittle. The middle group of products, *i.e.*, those made with CH_3 to Si ratios between 1.3 and 1.5, were soluble in hydrocarbons and alcohols, but as mentioned above were easily converted to gels by the action of dehydrating agents or by heating. After conversion to the gels the material was no longer soluble nor fusible.

Samples heated at 550° for 16 hours *in vacuo* and at 450° for one hour in hydrogen were unchanged beyond discoloration. Heating at 200° in air for one year caused no change, but at 300° in air disintegration occurred, perhaps as the authors stated through oxidation of an occasional methyl group. At 400° oxidation was more rapid. The properties of these resins were described in the original article.

Contemporaneously with the preceding there appeared a paper by Hyde and De Long[96] from the laboratories of the Corning Glass Works. Substituted silanes of the type R_3SiOH were dehydrated to form ethers or dimers (anhydrides). By the same process compounds of the type $R_2Si(OH)_2$ were able to form linear polymers with alternating silicon and oxygen atoms, while compounds of the type $RSi(OH)_3$ formed not only linear polymers but cross-linked aggregates as well. Attention was called to the strong tendency of the linear polymers to form trimers such as

$$
\begin{array}{ccc}
 & R_2 & \\
 & Si & \\
 \diagup & & \diagdown \\
O & & O \\
| & & | \\
R_2Si & & SiR_2 \\
 \diagdown & & \diagup \\
 & O &
\end{array}
$$
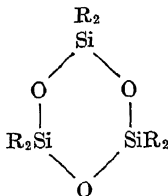
Hydrolysis of five dichlorosilanes under "mild" conditions led to the formation of low molecular weight products which, with one exception, were

liquids; diphenyldihydroxysilane formed a crystalline solid when dehydrated and trimerized. Cyclic polymers were also formed on the simultaneous hydrolysis and dehydration of ethylphenyldichlorosilane, dimethyldichlorosilane and diethyldichlorosilane. Higher polymers were formed by the removal of radicals, either by hydrolysis or oxidation. Thus the condensation product prepared from ethylphenyldichlorosilane was treated with aqueous hydrochloric acid, whereupon an evolution of benzene was observed accompanied by an increase in viscosity and the material eventually became quite tacky. Passing air through the system brought about the same general changes with the added formation of aldehydes, probably by oxidation of some of the alkyl radicals. Analysis showed that the ethylphenyl compound had preserved its cyclic trimeric structure but that R—Si linkages had in many cases gone over to Si—O—Si, as:

$$2Si—C_2H_5 + O \rightarrow Si—O—Si + RCHO$$
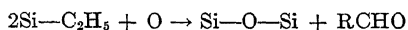
This work was described in considerable detail in the original paper. It was believed by the authors that, judging from a comparison of data, Kipping's tetrameric cyclic diphenyloxosilane was in reality a trimer[16, 20], as was the product isolated here. The formation of the cyclic trimer from the diol was found to be promoted by aqueous HCl, NH_4OH or some other alkali. Compounds thus prepared and condensed after hydrolysis were ethylphenyldichlorosilane, diethyldichlorosilane, methylphenyldichlorosilane, dimethyldichlorosilane and diphenyldichlorosilane.

C. A. Burkhard[329] found that the hydrolysis of diphenyldichlorosilane in homogeneous media, with water present in less than molar ratio to the silicon compound, yielded a polymerized linear silicone with two terminal chlorine atoms per molecule:

$$Cl—\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}——\left[O—\underset{\underset{C_6H_5}{|}}{\overset{\overset{C_6H_5}{|}}{Si}}——\right]_x Cl$$
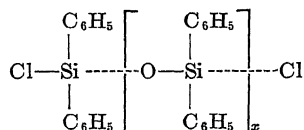
as well as $[(C_6H_5)_2SiO]_3$. A solution of diphenyldichlorosilane in toluene was dropped into a mixture of toluene, tertiary amyl alcohol and water. The temperature was kept at 25°, and thirty minutes were required to run in all of the silicon compound. The product was diphenyldihydroxysilane. An ether solution of this product was then dehydrated with 5 cc. of hydrochloric acid with three-hour reflux, yielding crystalline hexaphenylcyclotrisiloxane. Aqueous caustic added to a boiling solution of diphenyldihydroxysilane formed the corresponding tetramer.

Partial hydrolysis of diphenyldichlorosilane in water and dioxane gave 1,1,3,3-tetraphenyl-1,3-dichlorodisiloxane and some 1,1,3,3,5,5-hexaphenyl-1,5-dichlorotrisiloxane. These two products were easily subjected

to complete hydrolysis forming 1,1,3,3-tetraphenyl-1,3-dihydroxydisiloxane and 1,1,3,3,5,5-hexaphenyl-1,5-dihydroxytrisiloxane. Thermal dehydration of diphenyldihydroxysilane gave hexaphenylcyclotrisiloxane.

In 1946, Patnode and Wilcock[262] hydrolyzed dimethyldichlorosilane and certain related compounds in water at temperatures between 15° and 20°. The products were indeed varied, at least in the degree of polymerization shown. The empirical formula of these compounds was $[(CH_3)_2SiO]_x$. The yield of product with $x = 3$ was 0.5 per cent, with $x = 4$, 42 per cent, with $x = 5$, 6.7 per cent and with $x = 6$, 1.6 per cent. The relative proportions of these fractions could be changed by altering the hydrolytic agent. Hydrolysis in strong acid increased the percentages of low molecular weight products, as did the use of a water-miscible solvent. Most alkalies had the opposite effect.

From the residue, 49.2 per cent of the products, there were isolated polymers with $x = 7, 8$ and 9; this residue could, in turn, be pyrolyzed to give a 44 per cent yield of trimer. Treatment of the 49.2 per cent residue with concentrated sulfuric acid caused an increase in viscosity, sometimes even to the point where a rubber-like material was observed. Thus the tetramer was converted to a product in which the degree of polymerization rose to 37. Co-polymerization of hexamethyldisiloxane and cyclic polymeric dimethyloxosilane formed a polymer

$$(CH_3)_3Si-O-\left(-Si{\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{|}}}-O-\right)_x-Si(CH_3)_3.$$
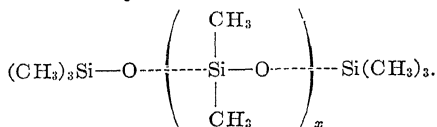
Co-hydrolysis of methyltrichlorosilane and trimethylchlorosilane followed by catalytic rearrangement gave $CH_3Si[-OSi(CH_3)_3]_3$.

Extensive investigation into the variation of polymer size with hydrolytic agent gave results varying from 20 to 98 per cent of the product boiling below 200°. Linear polymers were formed from mixtures of dimethyldichlorosilane and trimethylchlorosilane by hydrolysis and dehydration, the latter compound forming the terminal groups.

D. W. Scott[263] hydrolyzed a toluene solution of dimethyldichlorosilane and methyltrichlorosilane with a mixture of water, butyl alcohol and toluene. About two-thirds of the products were "volatile materials", but small amounts of more highly polymerized compounds were also formed. One product was reported as

$$\begin{array}{c}
Si(CH_3)_2 \\
\diagup \qquad \diagdown \\
O \qquad\qquad O \\
| \qquad\qquad\quad | \\
CH_3Si \qquad\quad SiCH_3 \\
\diagup \quad \diagdown \quad \diagup \quad \diagdown \\
(CH_3)_3SiO \qquad O \qquad OSi(CH_3)_3
\end{array}$$
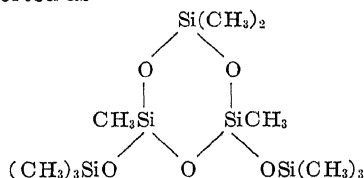
Alfrey, Honn and Mark[267] have presented some much-needed data regarding the variation of molecular weight and intrinsic viscosity with certain factors, such as purity of monomer and method of hydrolysis.

Diethyldichlorosilane was prepared by the action of ethylmagnesium bromide on tetrachlorosilane in molar proportions of 2.5 to 1. When hydrolyzed at 5°, using the dichloro compound once distilled, the molecular weight of the polymer was 815 and the intrinsic viscosity 0.021. Triply distilled monomer gave 410 and 0.015, respectively, and recrystallized monomer 250 and 0.008. Monomer hydrolyzed at 30° gave a polymerized material with molecular weight 430 and at 100°, 400. When hydrolysis and polymerization took place in the vapor phase, the molecular weight dropped to 360.

Thus diethyldichlorosilane, with ethyltrichlorosilane as impurity, hydrolyzed and condensed to an oil of moderate molecular weight and low volatility. This, when heated, showed an increase in molecular weight and intrinsic viscosity. If freed of ethyltrichlorosilane, the diethyl compound formed an oil of about half this molecular weight, as shown above, and some six times its volatility. Further heating caused an increase in intrinsic viscosity five times faster than the increase in molecular weight, probably because of the lesser chance of cross-linking in the purer sample.

Phosphorus pentoxide was found to react chemically and to form part of the polymer.

Sauer, Scheiber and Brewer[266] of the General Electric laboratories have reported hydrolysis products of methyldichlorosilane. These were linear compounds, prepared by "equilibration" with an excess of hexamethyldisiloxane.

Methyldichlorosilane was hydrolyzed in ice and water, giving a highly viscous oil which changed quickly to an opalescent, sticky, rubbery gel. When a water-soluble diluent was used, the percentage of low molecular weight polymers was increased, perhaps because the concentration of the polymerization catalyst, HCl, was thereby decreased. Products here were 2,4,6,8,-tetramethylcyclotetrasiloxane, 2,4,6,8,10-pentamethylcyclopentasiloxane and 2,4,6,8,10,12-hexamethylcyclohexasiloxane, in yields of 35.5, 16.7 and 4.4 per cent, respectively. It was believed that since no cyclic trimer was found there was "an enhanced reactivity of the siloxane linkage in these substances toward acid cleavage." Conversion to the rubbery solid was effected by contact between equal parts of water, hydrochloric acid and polymer.

Hexamethyldisiloxane and methyldichlorosilane were added to a mixture of ice and hexanes and from the products there were isolated heptamethyltrisiloxane, octamethyltetrasiloxane, 1,1,1,5,5,5-hexamethyl-3-trimethylsiloxytrisiloxane, nonamethyltetrasiloxane and decamethylhexasiloxane.

Another contribution, by Krieble and Elliott[571] in 1946, reported investigation of the tendency of certain carbon-silicon bonds to undergo fission in alkalies. Monomethylsilicones are very soluble in dilute sodium hydroxide solution; dimethylsilicones are less so, and tetramethyldisiloxanes are insoluble. None of these undergo cleavage at 100°. All react at 200° in an autoclave, giving methane and sodium silicate. The rate of cleavage varies as the number of oxygen atoms per molecule, but the solubility of the material may also be a factor.

Heptamethylchloromethylcyclotetrasiloxane was heated in potassium hydroxide and butyl alcohol. Methyl chloride was obtained along with infusible polymers; there was some cleavage of the carbon-chlorine bond as well. Pentamethylchloromethyldisiloxane hydrolyzed with aqueous alkali gave methyl chloride, hexamethyldisiloxane, octamethyltrisiloxane, dodecamethylpentasiloxane and decamethyltetrasiloxane. Pentamethyldichloromethyldisiloxane with potassium hydroxide formed methylene dichloride. Some of the carbon-chlorine linkages cleaved here also.

D. T. Hurd[357] prepared vinyltrichlorosilane and methylvinyldichlorosilane by chlorinating, and then abstracting HCl from ethyltrichlorosilane and from ethylmethyldichlorosilane, respectively.

Corning Glass laboratories[133] have recently carried out a series of preparations of successive polymers of condensation products with the general formula $[(CH_3)_2SiO]_x$. Dimethyldiethoxysilane was hydrolyzed in accordance with U. S. Patents 2380057[255] and 2384384[122], as was also dimethyldichlorosilane in accordance with U. S. Patent 2286763[104]. But the most efficient method of preparing lower polymers consisted finally in depolymerizing higher polymers *in vacuo* with sodium hydroxide catalyst; in this manner 90 per cent yields were obtained. The original article presented distillation curves showing the exhaustive nature of the work. Separation of polymers by distillation proved quite exact and complete. Compounds were prepared as indicated in Table 7. The work was continued by Hunter, Warrick, Hyde and Currie[427]. The low boiling points of methyl siloxane polymers as contrasted with the boiling points of saturated hydrocarbons of approximately the same molecular weight seemed to the authors to indicate a lack of strong intermolecular attractive forces. These compounds are also listed below.

Calingaert and co-workers[547] have presented additional data on radical interchange between tetraethylsilane, tetrapropylsilane and their mixed derivatives.

Markarova and Nesmeyanov[569] have reported that N_2O_3 does not react with tetraphenylsilane. An attempt has been made to bring about a reaction between tetraphenylsilane and boiling silver nitrate[554], but without success. Both Scott[537] and Wilcock[527] have reported additional disproportionations between types of organic compounds of silicon.

Wilcock[527] found that linear branched and cyclic types of polymers are present in "equilibriated polymers." As an apparent continuation of this work, Scott[537] has observed that the equilibrium constants covering certain "equilibration" of linear compounds are in agreement with the "current theories of polymer equilibria." For example, the number indicating average degree of polymerization of each of two chosen methylpolysiloxane mixtures was found to be 5.7 ± 0.3 and 4.3 ± 0.2 as determined by cryoscopic molecular weight measurements. Calculated values for the two were 5.6 and 4.2.

Scott summarized his work with the observation that the equilibrium constants "for a series of reactions involving cyclic species with four or more units per molecule vary in a regular manner with the number of units

Table 7.
Compounds $[(CH_3)_2SiO]_x$ (133).

$x =$	3	4	5	6	7	8
b.p.	133°	171°	204.5°	236°	147° (20 mm)	168° (20 mm)
m.p.	64.5°	17.4°	−44°	−3°	−32°	31.5°
d (25°)		0.9497	0.9531	0.9613	0.9664	
n (25°/D)		1.3935	1.3958	1.3996	1.4018	1.4039

Compounds $(CH_3)_3Si$—$(—OSi(CH_3)_2—)_xCH_3$ (427)

$x =$	1	2	3	4	5	6	7
b.p.	99.5°	152°	192°				
m.p.	−68°	−86°	−76°	−84°	−59°	−78°	−63°
d (25°/25°)	0.7606	0.8182	0.8516	0.8710	0.8873	0.9004	0.9078
n (25°)	1.3748	1.3822	1.3872	1.3902	1.3922	1.3940	1.3952

in the cyclic molecule." This he interpreted to mean that these cyclic "methylpolysiloxanes" are strain-free.

Mostly linear compounds were found when equilibration was carried out without diluent. Cyclic products were formed in an inert solvent such as carbon tetrachloride. Approach to equilibrium and its attainment were measured by determinations of viscosity.

Burkhard and Krieble[630] have reported a most interesting type of reaction, that of the addition of trichlorosilane to an ethylene or acetylene compound. Peroxides and ultraviolet light were the catalysts. Hydrogen from trichlorosilane added to one of the ethylenic carbons and trichlorosilicyl to the other, thus forming alkyltrichlorosilanes. Tests with caustic resulted in no evolution of hydrogen, indicating that no hydrogen is attached to silicon, and all the chlorine was easily hydrolyzed away, indicat-

ing that all chlorines are attached to silicon.   The following reactions were carried out:

$$iC_4H_8 + HSiCl_3 \rightarrow iC_4H_9SiCl_3$$
$$C_3H_7CH{=}CH_2 + HSiCl_3 \rightarrow C_5H_{11}SiCl_3$$
$$C_6H_{10} + HSiCl_3 \rightarrow C_6H_{11}SiCl_3$$
$$CH_2{=}CHSiCl_3 + HSiCl_3 \rightarrow (CH_2SiCl_3)_2$$
$$CH_2{=}CHCH_2SiCl_3 + HSiCl_3 \rightarrow CH_2(CH_2SiCl_3)_2$$
$$C_3H_7CH{=}CH_2 + CH_3SiHCl_2 \rightarrow C_5H_{11}Si(CH_3)Cl_2$$
$$C_2H_5CH{=}CHCH_3 + CH_3SiHCl_2 \rightarrow C_3H_7CH(CH_3)Si(CH_3)Cl_2$$
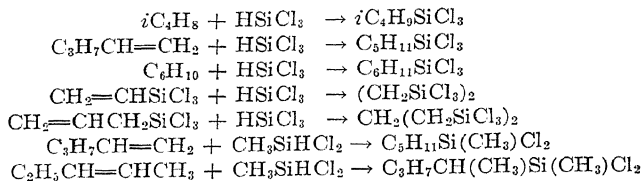
A free radical mechanism was considered most probable, since these reactions were catalyzed by peroxides and ultraviolet light.   Also, since styrene formed high-boiling products to the exclusion of the monomer, it was assumed that the following held true:

$$C_6H_5CH{=}CH_2 + SiCl_3 \rightarrow C_6H_5CHCH_2SiCl_3$$
$$C_6H_5CH{=}CH_2 + C_6H_5CHCH_2SiCl_3 \rightarrow C_6H_5CH\,CH_2CH(C_6H_5)CH_2SiCl_3$$
$$HSiCl_3 + C_6H_5CHCH_2SiCl_3 \rightarrow SiCl_3 + C_6H_5CH_2CH_2SiCl_3$$
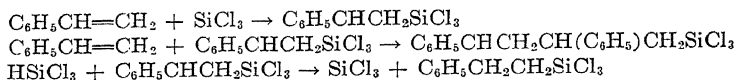
Of the two competing reactions, the first two seemed to prevail in the case of styrene.   Sommers, Pietrusza and Whitmore[633] have prepared octyltrichlorosilane by similar action in 99 per cent yields, influenced by the catalytic action of diacetyl peroxide.   The ultraviolet light-catalyzed reaction gave only 24 per cent yield.

Schlesinger and others[632] have reduced various chlorosilanes, substituting hydrogen for chlorine.   The hydrogenating agents were lithium aluminum hydride and lithium hydride.   There were prepared in this manner: ethylsilane, diethylsilane, propylsilane, dipropylsilane, butylsilane and phenylsilane.   These products were not particularly inflammable in air; they reacted slowly with water but vigorously with sodium hydroxide.

Discussions of electron diffraction have appeared.   Brockway and coworkers[369] have applied electron diffraction methods to a study of bond distances in the molecules of tetrachlorosilane and of tetrafluorosilane. The studies were also applied to methyltrichlorosilane, dimethyldichlorosilane and chlorotrifluorosilane[210], as well as to various methylchlorosilanes in addition to those mentioned above[392].   The molecular structures of tetramethylsilane and hexamethyldisilane were also studied[390, 391].

Giacomello[561] has reported on the crystalline structure of tetraphenylsilane.   Burkhard, Decker and Harker[330] studied the physical and crystallographic properties of octaphenylcyclotetrasiloxane, and Frevel and Hunter[331] have presented data on the physical structure and configuration of hexadecamethylcyclooctasiloxane.   Viscosities have been studied by D. F. Wilcock[346] and Hurd[433].

Sauer[434] and Warrick[439] independently made valuable contributions to the literature on atomic and molecular refractions. H. H. Anderson[658] has presented data covering the molar refraction of methylsilicon isothiocyanates with varying relative amounts of methyl and isothiocyanate from $Si(CH_3)_4$ to $Si(SCN)_4$. Any attempt to do justice to these and subsequent papers on this subject would require more space than this review permits. For further data on this subject there are the reports of Gilman and Clark[504] and of Smith[454]. Scott[437] has reported on osmotic pressures of silicon compounds and Sauer and Mead[436] on dielectric constants and dipole moments. Baker and others have also investigated dielectric constants[536], while Malatesta and Pizzotti[567, 568] have studied the dipole moments of organic compounds of silicon.

J. F. Hyde and associates[448] have presented data on the polymorphism of hexaphenylcyclotrisiloxane and related compounds.

Smith and Andrews[565] have investigated the heat capacity of tetraphenylsilane. Drew and Landquist[553] have studied the melting points of pure and mixed compounds such as AR_4, where "A" is an element of the fourth column of the Periodic Table. Entropy studies have been carried out by Aston and associates[534, 535].

Lewis and Newkirk[579] have successfully used Kinney's equations for the calculation of boiling points of organic compounds of silicon. The Raman spectra of silico-organic compounds have been studied by Rank and Bordner[549] and by Anderson[531]. Wall and Eddy[576] have reported observations on the "bond force constants" of tetramethylsilane. Silver has investigated[546] "the normal vibrations of molecules of the tetramethylmethane type including tetramethylsilane." The matter of free rotation in silicone molecules has been studied by Roth[544].

Young, Koehler and McKinney[657] conducted comparative infra-red studies on compounds of the type CR_4, SiR_4, SnR_4 and PbR_4.

Balis and Liebhafsky[455] have tested the flammability limits of dimethyldichlorosilane and methyltrichlorosilane in air. The value for the first compound is 3.4 per cent (± 0.1) and for the second 7.6 per cent (± 0.3). Hydrochloric acid had no effect, but tetrachlorosilane caused a slight increase in the lower limit of the first compound.

Clapp[578] has shown that, after irradiation with ultraviolet light, tetraphenylsilane and tetra-*p*-tolylsilane show bright green phosphorescence over a period of twenty seconds. Tetra-*p*-diphenylsilane does not give this reaction.

Gilman and co-workers[401] have presented a new method for the determination of organic silicon by the use of perchloric acid.

Several reviews have been published during this period. A review of the chemistry of metallo-organic compounds, including those of silicon,

appeared in this country in 1943[417]. Harold Hausman[290] of the General Luminescent Corporation of Chicago has written a comprehensive and easily understandable short survey of this field. A more detailed and technical covering was given by Rochow in 1946[349] and by a group of authors in the following year[529].

Any summary of the preparation of organic compounds of silicon at moderate temperatures must of necessity call attention to the extreme versatility of these reactions. Any metal which will form a metallo-organic compound which is soluble in some inert solvent seems to be acceptable. This includes magnesium as of first rank, then mercury and lithium. Gilliam and associates[95] found that dimethylmercury and dimethylzinc did not react with tetrachlorosilane.

Hyde and co-workers have shown the feasibility of oxidizing stable cyclic silicon compounds in such a way that organic radicals are burned off the silicon and siloxane linkages set up. The strong tendency of these siloxanes to polymerize to cyclic trimers should also be noted.

Jones, Thomas, Pritchard and Bowden[661] prepared several polyethers for the purpose of determining the atomic parachor of silicon. It was concluded that the atomic parachor of silicon varied considerably with the complexity of the compound under observation. The ethers were prepared by the action of the proper alcohol on tetrachlorosilane, for instance ethylene chlorohydrin and 1,3-dichloropropanol-1.

Whitmore pointed out certain reactions of silicon and corresponding carbon compounds which could most easily be explained by certain assumptions regarding the relative size of the respective positive atomic nuclei. Whatever may be felt, however, with regard to the size of the silicon nucleus and its effect on the chemical reactions of the atom, there must still be at least a tendency, similar to that existing for carbon, to form the conventional five- and six-membered rings.

The general susceptibility of organic radicals to burning can be offset by the introduction of halogen in place of hydrogen in selected positions. In general, however, the carbon-silicon bond is unusually stable.

Some investigators have not been successful in attempts to cause sodium to react with silicon-fluorine bonds[171], but Wiley[223] has obtained a patent for this type of reaction.

It is interesting to note also that polysilicon compounds, such as hexachlorodisilane and octachlorotrisilane, react in accordance with the Wurtz-Fittig scheme to form derivatives of silane itself[93].

Molar ratios are always of great importance, not only in the formation of the organic compounds through the action of metalloorganic compounds but even more in the hydrolysis of these halides.

Table 8

Organic Compounds of Silicon Prepared at Moderate Temperatures
(classified as to the reagents used in their synthesis)

METALS

$(CH_3)_3SiCH_2MgCl$ (259); $(C_6H_5)_3SiH$, $(C_6H_5)_3SiLi$, $(C_6H_5)_3SiNa$, $(C_6H_5)_3SiSi(C_6H_5)_3$ (324)

(OXYGEN)

Polymeric materials (96)

HALOGENS

$CH_3Si(CH_2Cl)Cl_2$, $CH_3Si(CHCl_2)Cl_2$, $CH_3Si(CCl_3)Cl_2$, $CH_3Si(CH_2Cl)_2Cl$, $(CH_3)_2Si(CHCl_2)Cl$, $(CH_3)_2Si(CH_2Cl)Cl$ (451); $C_2H_5CHClSiCl_3$, $CH_3CHClCH_2SiCl_3$, $CH_2ClCH_2CH_2SiCl_3$ (261); $(CH_3)_3SiCl$ (230); $(CH_3)_3SiCH_2Cl$, $(CH_3)_3SiCH_2I$ (259); $CH_3CHClSi(C_2H_5)_2Cl$, $CH_2ClCH_2Si(C_2H_5)_2Cl$, $CH_3CHClSi(C_2H_5)_2F$, $CH_2ClCH_2Si(C_2H_5)_2F$ (363); $C_6H_5CHClSiCl_3$ (260); $(C_2H_5)_3SiCH_2CH_2Cl$ (221, 260); $(C_2H_5)_3SiCHClCH_3$, $(C_6H_5)_3SiBr$ (324).

WATER

$(CH_3)_3SiOH$ (438); $(C_2H_5)_2Si(OH)_2$ (267, 314); $(C_2H_5)_3SiOH$ (438); $(C_6H_5)_3SiOH$ (449); $(CH_3)_2Si(CH_2Cl)OSi(CH_3)_2CH_2Cl$, $(CH_3)_3SiOSi(CH_3)_2CH_2Cl$, $(CH_3)_3SiOSi(CH_3)_3$ (451); $(C_2H_5)_3SiOSi(C_2H_5)_3$ (363); $C_{24}H_{22}Si_2O_3$ (329); $[(CH_3)_2SiO]_3$ (262); $C_6H_{19}Si_3O_2$ (266); $[(C_6H_5)_2SiO]_3$, $C_{36}H_{32}Si_3O_4$ (329); $(CH_3SiHO)_4$ (266); $C_8H_{26}Si_4O_3$ (266); $((CH_3)_2SiO)_4$ (262); $C_9H_{28}Si_4O_4$ (263); $CH_3Si(OSi(CH_3)_3)_3$ (262); $(C_6H_5)_2Si(Cl)—$ $(—OSi(C_6H_5)_2—)_3Cl$ (329); $(CH_3SiHO)_5$ (266); $[(CH_3)_2SiO]_5$ (262); $C_{10}H_{30}Si_5O_5$ (263); $C_{12}H_{36}Si_5O_4$ (266); $(C_6H_5)_2Si(Cl)—(—OSi(C_6H_5)_2—)_4Cl$ (329); $C_{10}H_{34}Si_6O_6$ (266); $[(CH_3)_2SiO]_6$, $[(CH_3)_2SiO]_7$, $[(CH_3)_2SiO]_8$, $[(CH_3)_2SiO]_9$ (262); $(CH_3SiO_{1.5})_x$ (92, 133); $(CH_2ClCH_2SiO_{1.5})_x$ (271)

DEHYDRATION

$(CH_3)_3SiOSi(CH_3)_3$ (309, 438); $(C_6H_5)_3SiOSi(C_6H_5)_3$, $[(CH_3)_2SiO]_3$, $(C_2H_5Si(CH_3)O)_3$, $[(C_2H_5)_2SiO]_3$, $(C_6H_5Si(C_2H_5)O)_3$ (96); $[(C_6H_5)_2SiO]_3$ (96, 448); $(RSiO_{1.5})_x$ (96)

HYDROHALOGEN ACIDS

$(CH_3)_3SiF$ (438); $Si(CH_3)_4$ (259); $(C_2H_5)_3SiF$, $(C_2H_5)_3SiCl$ (410, 453); $(C_2H_5)_3SiBr$ (410)

CAUSTIC ALKALIES

$(CH_3)_3SiOH$, $(C_2H_5)_3SiOH$ (438); $Si(ONa)_4$ (271); $(C_2H_5)_3SiONa$ (438); $(C_2H_5)_3SiCH_2CH_2OH$ (221)

SALTS

CH_3SiF_3 (397, 432); CH_3SiF_2Cl, CH_3SiFCl_2, (397); $(CH_3)_2SiF_2$ (398, 432); $(CH_3)_2SiFCl$ 398); $C_2H_5SiF_3$ (291, 395); $C_2H_5SiF_2Cl$, $C_2H_5SiFCl_2$ (395); $(CH_3)_3SiF$ (398, 432); $(C_3H_7SiF_3$, $C_3H_7SiF_2Cl$, $C_3H_7SiFCl_2$ (396); $iC_3H_7SiF_3$, $iC_3H_7SiF_2Cl$, $iC_3H_7SiFCl_2$ (399); $(CH_3)_3SiCH_2HgCl$ (260); $(C_2H_5)_2SiF_2$ (291); $C_4H_9SiF_3$, $C_4H_9SiF_2Cl$, $C_4H_9SiFCl_2$ (400); $CH_3CH(HgCl)Si(CH_3)_3$ (260); $(C_2H_5)_3SiF$, $C_6H_5SiF_3$ (291); $CH_3COOCH_2CH_2Si(C_2H_5)_3$ (221); $(C_6H_5)_2SiF_2$, $(C_6H_5)_3SiF$ (291, 324)

Table 8—*Concluded*

GRIGNARD REAGENTS

CH_3SiCl_3 (92, 397); $(CH_3)_2SiCl_2$ (92, 398); $C_2H_5SiCl_3$ (395); $(CH_3)_3SiH$ (230); $(CH_3)_3SiCl$ (315, 398); $C_3H_7SiCl_3$ (396); $iC_3H_7SiCl_3$ (399); $(CH_3)_3SiOH$ (309); $Si(CH_3)_4$ (271); $(CH_3)_2Si(C_2H_5)Cl$, $(CH_3)_2Si(C_2H_5)Br$ (446); $(C_2H_5)_2SiCl_2$ (267); $C_4H_9SiCl_3$ (400); $(C_2H_5)_2SiHCH_3$, $(CH_3)_2SiHC_3H_7$ (645); $CH_3CHClSi(CH_3)_3$, $C_5H_{11}SiCl_3$, $(CH_3)_3SiC_2H_5$, $(CH_3)_3SiCH_2HgCH_3$ (258); $(C_2H_5)_3SiH$ (85, 362, 645); $C_6H_5SiHCl_2$ (446); $(C_2H_5)_3SiF$ (171); $C_6H_{13}SiCl_3$, $(CH_3)_3SiC_3H_7$, $C_7H_{15}SiCl_3$, $(CH_3)_3SiC_4H_9$ (258, 506); $(C_2H_5)_3SiCH_3$ (258, 438); $CH_3CHClSi(C_2H_5)_2CH_3$ (363); $(C_3H_7)_2SiHCH_3$ (645); $Si(C_2H_5)_4$ (88, 258, 271, 422); $(CH_3)_3SiC_5H_{11}$, $(C_2H_5)_3SiC_3H_7$, $(CH_3)_3SiC_6H_{13}$ (258); $(C_3H_7)_3SiF$ (171); $(C_3H_7)_3SiH$ (645); $(CH_3)_3SiC_6H_4Cl$, $(CH_3)_3SiC_6H_4Br$ (421); $(C_2H_5)_3SiC_4H_9$, $(CH_3)_3SiC_7H_{15}$, $C_{10}H_{21}SiCl_3$, $(C_2H_5)_3SiC_5H_{11}$ (258); $(CH_3)_3SiC_8H_{17}$ (258, 633); $(C_4H_9)_3SiF$ (171); $Si(C_3H_7)_4$ (88); $(CH\equiv C)_3SiOSi(C\equiv CH)_3$ (224); $CH_3CHClSi(C_2H_5)_2C_6H_5$ (363); $(C_2H_5)_3SiC_6H_{13}$, $C_{12}H_{25}SiCl_3$, $(C_2H_5)_3SiC_7H_{15}$, $(CH_3)_3SiC_{10}H_{21}$, $(C_2H_5)_3SiC_8H_{17}$, $C_{14}H_{29}SiCl_3$, $(CH_3)_3SiC_{12}H_{25}$, $(C_2H_5)_3SiC_{10}H_{21}$, $(CH_3)_3SiC_{14}H_{29}$ (258); $(C_6H_5)_3SiOH$, $Si(C_6H_5)_4$ (88); $Si(C_6H_4CH_3-m)_4$, $Si(C_6H_4CH_3-p)_4$ (91); $(C_2H_5)_3SiSi(C_2H_5)_3$, $(C_3H_7)_3SiSi(C_3H_7)_3$, $(C_6H_5)_3SiSi(C_6H_5)_3$, $(C_6H_5)_3SiOSi(C_6H_5)_3$ (88); $(C_6H_5CH_2)_3SiSi(CH_2C_6H_5)_3$ (91); $(CH_3)_3SiCH_2Si(CH_3)_3$, $(CH_3)_3SiCH_2Si(CH_3)_2CH_2Si(CH_3)_3$, $(CH_3)_3SiCH_2Si(CH_3)_2CH_2Cl$ (505)

TRIMETHYLTANNIC CHLORIDE

$(C_6H_5)_3SiSn(CH_3)_3$ (324)

PHENYL HALIDES

$Si(C_6H_5)_4$ (324)

SODIUM + ORGANIC HALIDES

$Si(C_2H_5)_4$, $Si(C_5H_{11})_4$ (93); $Si(C_6H_5)_4$ (88, 91, 93); $Si(C_6H_4CH_3-p)_4$ (93); $(C_6H_5)_3SiSi(C_6H_5)_3$ (91, 98); $(C_6H_5)_3SiOSi(C_6H_5)_3$ (91); $(p-CH_3C_6H_4)_3SiOSi(C_6H_4CH_3)_3$ (88); $(C_6H_5CH_2)_3SiSi(CH_2C_6H_5)_3$ (91)

ALKYL LITHIUM COMPOUNDS

$(C_2H_5)_3SiCH_3$ (338); $Si(C_2H_5)_4$ (449); $(C_2H_5)_3SiC_4H_9$, $(C_2H_5)_3SiC_3H_7$, $(C_2H_5)_3SiC_6H_5$ (362); $tC_4H_9SiCl_3$ (506); $(iC_3H_7)_3SiCl$, $(iC_3H_7)_3SiOC_2H_5$, $(iC_3H_7)_3SiC_6H_5$ (522); $Si(C_4H_9)_4$, $(C_6H_5)_3SiCl$, $Si(C_6H_5)_4$, $(C_6H_5)_3SiC_6H_4CH_3-p$, $(C_6H_5)_2Si(C_6H_4CH_3-p)_2$ (449, 504).

SULFURIC ACID

$[(C_2H_5)_3SiO]_2SO_2$ (438, 453)

ACETIC ANHYDRIDE

$CH_3COOSi(C_2H_5)_3$ (438)

INTERCHANGE

$(C_2H_5)_3SiCl$, $(C_2H_5)_2SiH_2$, $(C_2H_5)_2SiHCl$ (582); $Si(C_2H_5)_4$, $(C_2H_5)_3SiC_3H_7$, $(C_2H_5)_2Si(C_3H_7)_2$, $C_2H_5Si(C_2H_7)_3$, $Si(C_3H_7)_4$ (547)

METALLIC HYDRIDES

$C_2H_5SiH_3$, $C_3H_7SiH_3$, $(C_2H_5)_2SiH_2$, $(C_3H_7)_2SiH_2$, $C_6H_5SiH_3$, $C_4H_9SiH_3$ (632)

ADDITION TO OLEFINES OR ACETYLENES

$iC_4H_9SiCl_3$, $C_5H_{11}SiCl_3$, $C_6H_{11}SiCl_3$, $C_6H_{11}Si(CH_3)Cl_2$, $C_3H_7CH(CH_3)Si(CH_3)Cl_2$ (630); $C_8H_{17}SiCl_3$ (633); $(CH_2SiCl_3)_2$, $CH_2(CH_2SiCl_3)_2$ (630)

Chapter 5

Organic Compounds of Silicon Prepared at Moderate Temperatures

(Patent Literature)

The patent literature which appeared parallel to the papers discussed in Chapter 4 is of such volume that it has been deemed advisable to assign it a separate chapter, with subdivisions according to the source of the material. The first section of this chapter will therefore be devoted to products of the General Electric laboratories, the second to those from Corning Glass Works and allied organizations, and the third to the remainder of the current patent literature covering organic compounds of silicon prepared at moderate temperatures.

General Electric's patents preceded others in this country chronologically.

General Electric Group

U. S. Patent 2258218 (1941)

This patent (99) "Methyl Silicones and Related Products" was General Electric's earliest. It covered " . . . polymeric bodies comprising chemical compounds o f silicon, oxygen and at least one methyl group attached directly to silicon" and as specified farther on " . . . polymers of methyl silicon and of related compounds in which the methyl groups are replaced in part by oxygen."

In Example 1, methylmagnesium bromide and tetrachlorosilane, both in anhydrous ether, reacted in molar ratio of 1.75/1.00 at an initial temperature of $-20°$ or lower. The temperature of the system was not allowed to rise above 0°. A mixture of methyltrichlorosilane and dimethyldichlorosilane resulted; this mixture was hydrolyzed by the action of cracked ice to a viscous liquid which could then be further condensed by heating from 100° to 200°. When the liquid reaction product was kept at 200° for 48 hours there resulted a clear, colorless, odorless, horny solid, believed to be a polysiloxane, possibly with cross linkages. Example 2 specified a molar ratio of 1/1, giving mostly methyltrichlorosilane. The 2.25/1.00 ratio in Example 3 gave chiefly dimethyldichlorosilane, but some mono- and trimethyl compounds also were found.

A series of twenty claims was listed in more or less detail covering the uses of these compounds as well as their preparation.

77

U. S. Patent 2258219 (1941)

The second patent (100) of this group, covered the preparation of halogenated polymerized oxosilanes with two like groups, as for instance ditrichlorophenyloxosilane, and with two unlike groups, as methylchlorophenyloxosilane. It is of interest to note that one of the chief advantages of this type of halogenated product lies in its reduced tendency to burn. Whereas diphenyloxosilane, polymerized, burns readily with the application of the flame, the introduction of one, two or three chlorines in each benzene ring progressively reduces this tendency. Rochow covered the right to halogenate to the limit, but stated that introduction of halogen atoms beyond the point where flammability had been eliminated would not be feasible or profitable.

On the application of heat these halogenated polymers changed progressively from the more soluble thermoplastic materials, some fusing between 50° and 60°, to the hard, brittle, resistant types with points of fusion around 250°. All this was brought about by continued heating between 175° and 200°.

Table 9.

	"A"	"B"
Example 1	0.75	yellow, horny
Example 2	1.00	sticky, resinous
Example 3	1.25	resinous to rubbery

"A" = ratio Grignard/SiCl₄.
"B" = nature of hydrolysis product.

The work leading to halogenation was very interesting as synthetic organic chemistry, especially iodination with iodine pentoxide. This added to the evidence for the well known stability of the carbon-silicon bond.

U. S. Patent 2258220 (1941)

The general coverage in this patent (101) was new compounds and in particular "new and useful resinous materials" of the general formula

$$(C_2H_5)_x SiO_{(4-x)/2}$$
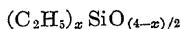
with x varying between 0.5 and 1.5. These are "solid or semi-solid bodies or thick, syrupy, almost non-flowing liquids." Particular attention should be paid to the method of hydrolyzing dihalogenosilanes covered in these patents. It is believed that many of the physical properties of the resulting polymers are strongly influenced by a slight variation in method of hydrolysis. Coating compositions were also included among the claims.

U. S. Patent 2258221 (1941)

This patent (102) specifically covered aroxysilicones with radicals of the type R—O—R'—attached to silicon. "R" may or may not be halogenated. It is interesting to read of the formation of the Grignard reagent in dry ethyl ether from an organic halide which is itself a high molecular weight ether. The latter must be sufficiently unreactive not to co-ordinate or otherwise allow itself to be removed from availability. Mono- or diderivatives were thus formed whose cold solutions were hydrolyzed on contact with cracked ice. Condensation to the silicone was effected by heat at 110° for four hours. Further heating at 175° developed a hard silicone which contained 1.09 *p*-phenoxyphenyl groups per silicon atom. Again it was found that the presence of one or more halogen atoms in the silicone materially reduced its flammability. The presence of three such halogens on one aromatic ring was desirable for this purpose. Some of the claims covered applications as insulating material, etc.

Table 10. Molar ratios.

	C_6H_5	CH_3	Si
Before	0.71	1.15	1.00
After	0.44	0.66	1.00

U. S. Patent 2258222 (1941)

This patent (103) covered methyl aryl silicones and certain products of utilization.

As noted before, the product at the stage of hydrolysis was soluble in organic solvents. The method of further dehydration, new in some respects, comprised boiling in toluene to eliminate still more water of condensation. The usual heating at 175° followed. The following table shows the radical or atomic ratios of phenyl, methyl and silicon as used in the typical reactions described and the ratios as they appeared in the final products. Halogens attached to carbon imparted flame resistance here as in other instances.

U. S. Patent 2286763 (1942)

In reading this patent (104) attention should be directed to the use of anhydrous dibutyl ether as a solvent. Obviously the use of higher-boiling ethers makes possible the application of higher temperatures than could be attained by the use of diethyl ether, although it was expressly stated that "larger yields of purer materials are obtained with ethyl ether." Activated alumina was used in the drying tube to keep the system anhydrous.

U. S. Patent 2352974 (1944)

U. S. Patent 2352974 (111) covered specifically organic silicon compounds in which "a plurality of divalent organic radicals are each linked to two separate (different) silicon atoms." The emphasis was obviously on the concept of divalence. It was further pointed out that combinations of these divalent radicals with monovalent radicals are possible. This type of condensation might make use of two monovalent radicals for every one which would be divalent, and with such a large percentage of the former, the compound would lose much of its ability to form long chains. It was suggested that the average number of monovalent radicals may be less than twice the number of divalent. These specifications did not exclude the possibility of siloxane linkages existing as well as the others. The condensation product was "a soft brown resin," as described at one point. Radicals suggested included $-(CH_2)_x-$, $-C_6H_4-$, etc. Applications of these products were also discussed.

U. S. Patent 2371068 (1945)

"New and improved methods for effecting condensation or dehydration of organo-silicols, including the products thereby obtained," are covered in this patent (114), that is, compounds of the type $R_xSi(OH)_{4-x}$. It was not required that in any one system just one value of x should be represented; for instance, R_3SiOH, $R_2Si(OH)_2$ and $RSi(OH)_3$ might exist together. Obviously, however, the physical properties of the product, especially with respect to cross linkages, would vary with the spread of values represented by x.

Heat dehydration and polymerization did not always give desirable results, since occasionally the lower molecular weight products volatilized and were partially lost. This was especially true in connection with compounds of a high CH_3/OH ratio. A long list of acceptable dehydrating agents is presented on the first page of this patent. Ordinarily from 0.1 to 20 per cent by weight of these agents may be used.

In Example 1, 10 or 20 per cent of ethyl borate was suggested, and in Example 2, antimony pentachloride, sulfuric acid or ethylene diamine to dehydrate.

U. S. Patent 2381366 (1945)

A new type of silicone was covered here (121)—new at least to patent literature—the type of compound known as a linear siloxane. J. F. Hyde covered cyclic siloxanes but Patnode of General Electric has described the linear type.

The method was conventional in principle but adapted to the ends in view, namely hydrolysis of a dichlorosilane to a dihydroxysilane and sub-

sequent dehydration to a linear polymer. A falling temperature was noticed during the reaction as hydrochloric acid boiled off. Hydrolysis of the ether solution of dimethyldichlorosilane was carried out by the action of a mixture of water and dioxane. This gave a one-phase system when the aqueous solution was added dropwise. Patnode called attention to the fact that hydrolysis of dimethyldichlorosilane in a two-phase system (U. S. Patent 2258218) gave completely hydrolyzed products, whereas here two chlorines were left, one at each end of the chain.

U. S. Patent 2383817 (1945)

This patent (499) covered the formation of compounds with more or less regularly recurring Si—C—Si units. Thus polyfunctional Grignard reagents, as $R'(MgX)_2$, reacted with a halogenated silane to form these linear and cross-linked polymeric compounds.

U. S. Patent 2383827 (1945)

Murray M. Sprung, assigning to General Electric (378), covered the preparation of a "methylphenylsilicone resin" by the interaction of a mixture of $SiCl_4$, $C_6H_5SiCl_3$, $(C_6H_5)_2SiCl_2$, CH_3SiCl_3 and $(CH_3)_2SiCl_2$ with a hydrolyzing mixture consisting of two parts by weight of tertiary amyl alcohol, one of toluene, and ten of water. The mixture of chlorides had previously been dissolved in toluene. Certainly there should have been sufficient variety in the realm of chlorides to form any number of linkages including those connecting chain to chain. Among the claims herein stated there appeared one covering the heating of a solution of a silicone resin in an aromatic hydrocarbon with a hydrated metal salt. At least 10 per cent of the non-resinous components of the system distilled off.

U. S. Patent 2386259 (1945)

Herein (379) will be found descriptions of the waterproofing of materials by treating them with the hydrolysis products of CH_3SiHCl_2 and CH_3SiHBr_2. Aging of the treated materials increased their efficiency, and catalytic agents for this aging were listed.

U. S. Patent 2388299 (1965)

This patent (380) covered the use of organohalogenosilanes as coating materials for wax molds. By their application water-repelling properties were enhanced and the products rendered generally more durable.

U. S. Patent 2388575 (1945)

Another U. S. Patent (381) of the same date described the resolution of mixtures of chlorosilanes; for instance, tetrachlorosilane formed an azeo-

trope with trimethylchlorosilane. From this azeotrope and the mixture with other methylchlorosilanes, tetrachlorosilane could be separated by adding a nitrile, as acetonitrile, and distilling. The system resolved itself into an azeotrope of tetrachlorosilane and acetonitrile and other fractions yielding the methylchlorosilanes.

U. S. Patent 2389477 (1945)

This patent (248) ". . .relates to polysiloxane resins of improved aging and curing characteristics and to a method of preparing such resins." The halogenated silanes were not necessarily all the same in any one system. The ultimate hydrolysis products of these chlorinated silanes, probably of the types R_3SiOH, $R_2Si(OH)_2$ and $RSi(OH)_3$, averaged between one and two radicals per silicon atom. These were treated, in inert solution, and at elevated temperatures, with a polymerization and dehydration catalyst. A hydrated salt such as ferric chloride seemed to be an essential constituent of this catalyst.

U. S. Patent 2390378 (1945)

Marsden's patent, (247) assigned to General Electric (U. S. Patent 2390378) covered the hydrolysis of alkyl polychlorosilanes to alkyl polyhydroxysilanes. Mixtures of the former with tetrachlorosilane in some inert solvent such as methyl propyl ketone were also used. Hydrolysis was accomplished with water below 30° but above 0° where ice might form.

U. S. Patent 2392713 (1946)

In 1946 appeared a contribution (382) referring to the process of preparing "dimethyl silicone elastomers." Co-pending applications had covered the preparation of silicone elastomers, and here mention was made of the formation, in this process, of cured or partially cured scrap material. This patent covers the treatment of the scrap material with dimethyldihalogenosilanes, with formation of a sticky, gummy mass which could be worked up to a point where it was indistinguishable from the fresh silicone gum. Benzoyl peroxide was a catalyst in this reconversion.

U. S. Patent 2394040 (1946)

The tensile strength of asbestos fiber was increased nearly three-fold by the method described in this patent (383). The probable chemical reaction by which this increase was brought about is also interesting and is reproduced below. Asbestos was represented in the patent as having the structural unit

$$=Si(OMgOH)_2$$

which reacted with tetrachlorosilane to form, first the oxide

$$=\text{Si} \underset{\text{O}-\text{Mg}}{\overset{\text{O}-\text{Mg}}{\diagdown\diagup}} \text{O}$$
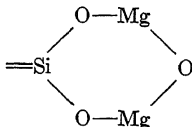
and then long chain units as

$$-\text{Si}-\text{O}-\text{Mg}-\text{O}-\text{Si}-.$$

There were improved tear resistance and increased density in the final product as contrasted with untreated asbestos.

U. S. Patent 2398672 (1946)

This patent (270) covered (1) preparation of silicone resins, (2) an improved method of hydrolyzing organic silicon halides, (3) a practical method for hydrolyzing mixtures of chlorinated silanes, etc., and finally (4) a method of hydrolyzing mixtures using non-inflammable and inexpensive solvents.

The most significant part of this patent was a series of statements covering the relative properties of films prepared by these methods and of others made from ether solutions. For instance, in Example 2, a mixture of $(CH_3)_2SiCl_2$, CH_3SiCl_3 and $SiCl_4$ in toluene was hydrolyzed (exothermal reaction) by a mixture of ice, water and n-butanol. Films prepared from this resin "on a matted glass fiber base exhibited only a few cracks after being heated for five days at 200°", while comparable films in whose preparation ether had been used as a solvent, cracked badly or crazed after heating overnight at 200°.

Nearly two pages are allotted in this patent to a detailed discussion of optimum concentrations, etc., for effecting hydrolysis and recombination with loss of water to form polysiloxanes or silicones. Gel formation during hydrolysis was reduced.

U. S. Patent 2405041 (1946)

This patent (385), dated July 30, 1946, covers the preparation of various "methyl polysiloxane resins" by an extraction process. Nitroparaffins were found suitable, as solvents, particularly those with 2, 3 or 4 carbon atoms per molecule. The extraction of polymerized hydroxyoxosilanes was carried out with hot materials; then as the extract cooled a precipitate formed.

U. S. Patent 2406605 (1946)

Hurd has assigned to General Electric this patent (386) covering the hydrogenation of halogenosilanes. It will be noted that yields of products,

for instance H_2SiCl_2 and $HSiCl_3$ from $SiCl_4$, are not large.   Nevertheless the reaction has possibilities.

U. S. Patent 2406621 (1946)

Methods of hydrolyzing halogenated silanes are covered here (387). This patent is a continuation of the work of Robert O. Sauer (270).

U. S. Patent 2421653 (1947)

"Halosilanes and organopolysiloxanes" equilibriate (524) giving mixed polyhaloorganosiloxanes. Thus in the copper liner of a steel bomb, dimethyldichlorosilane and a dimethylsiloxane interact. The products have methyls and chlorines in the same molecule, for instance as $(CH_3)_3$ $SiOSi(CH_3)_2Cl$, b.p. 118.6°–119.6° (758 mm) and $(CH_3)_3SiOSiCl_3$, b.p. 127.0°–127.3° (754 mm).

U. S. Patent 2426912 (1947)

General Electric[662] has covered the hydrolysis of dimethyldihalogenosilanes by pouring on the surface of a swirling solution of an electrolyte.

To summarize General Electric's patents requires mention of work on the effect of reagent ratios on the nature of products. U. S. Patent 2258218 (99) describes a Grignard/silicon ratio of 1.00 and its use in a reaction which formed methyltrichlorosilane. A ratio of 1.75 gave the same compound plus dimethyldichlorosilane, while a ratio of 2.25 caused the formation of some trimethylchlorosilane. U. S. Patent 2258220 (101) listed horny products arising from a reaction with Grignard reagent and silicon present in the ratio of 0.75/1.00, sticky resins from the use of a 1.00 value, and resinous to rubbery with 1.25. Again, U. S. Patent 2258222 (103), covering the action of a mixture of methyl and phenyl Grignard reagents, reported that 57 per cent of the methyl groups were found in the final product and 62 per cent of the phenyl. The use of halogenated radicals to reduce tendency to burn was covered in U. S. Patents 2258219 (100) and 2258221 (102). Ethereal radicals such as *p*-phenoxyphenyl are listed in 2258221 (102) and the use of dibutyl ether for higher temperatures was covered in 2286763 (104). Diradicals from di-Grignard reagents were described in U. S. Patent 2352974 (111). Extensive and thorough work on hydrolytic reactions was described in a series of patents 2371068 (114), 2381366 (121), 2389477 (248) and 2390378 (247). The preparation of films was reported in U. S. Patent 2398673 (270).

CORNING GLASS GROUP

Although the patents listed in this section began at a slightly later date than those preceding, their content is none the less fundamental and cm-

bracing. This second group originated in the laboratories of the Corning Glass Co. and its associates.

British Patent 561136 (1944)

This patent (441) covers "organo-silicon compounds and polymers thereof, and ... the use of such polymers in the production of electrical insulating and protective coatings, plastics, impregnating agents and fillers for fabrics and fibrous agents."

Table 11. Compounds Prepared at Moderate Temperatures: Methods Covered by General Electric Patents.

HALOGENS

$Cl_4C_6HSi(CH_3)Cl_2$, $(IC_6H_4)_2SiCl_2$, $(Cl_3C_6H_2)_2SiCl_2$ (100)

WATER

$CH_3Si(OH)_3$, $(CH_3)_2Si(OH)_2$, $(CH_3)_3SiOH$ (99, 247, 248); $(C_2H_5)_2SiO$ (101); $Cl_3C_6H_2Si$-$(CH_3)O$, $Cl_4C_6HSi(CH_3)(OH)_2$ (100); $C_6H_5Si(CH_3)(OH)_2$, $C_6H_5Si(CH_3)O$ (103); $(Cl_3C_6H_2)_2SiO$, $(BrC_6H_4)_2SiO$, $(p\text{-}FC_6H_4)_2Si(OH)_2$, $(p\text{-}FC_6H_4)_2SiO$, $(IC_6H_4)_2SiO$ (100); $p\text{-}C_6H_5C_6H_4SiCl_3$ (102); $(CH_3C_6H_3Cl)_2SiO$ (100); $(p\text{-}C_6H_5OC_6H_4)_2Si(OH)_2$ (102); $ClSi(CH_3)_2OSi(CH_3)_2Cl$ (121); $[(CH_3)_2SiO]_2$(99, 114); $ClSi(C_2H_5)_2OSi(C_2H_5)_2$-Cl, $BrSi(C_2H_5)_2OSi(C_2H_5)_2Br$ (121); $C_6H_5Si(CH_3)(OH)OSi(C_6H_5)(CH_3)OH$ (103); $HOSi(C_6H_2Cl_3)_2OSi(C_6H_2Cl_3)_2OH$ (100); $HOSi(C_6H_4OC_6H_5\text{-}p)_2OSi(C_6H_4OC_6H_5\text{-}p)_2$-OH (102); $ClSi(CH_3)_2$—[—$OSi(CH_3)_2]_2Cl$ (121); $[(CH_3)_2SiO]_3$ (99, 114); $HOSi(CH_3)$$(C_6H_5)$—[—$OSi(CH_3)(C_6H_5)$—$]_2OH$ (103); $HOSi(C_6H_2Cl_3)_2$—[—$OSi(C_6H_2Cl_3)_2$—$]_2OH$, $[C_6H_2Cl_3)_2SiO]_3$ (100); $HOSi(C_6H_4OC_6H_5)_2$—[—$OSi(C_6H_4OC_6H_5)_2$—$]_2OH$, $[(p\text{-}C_6H_5OC_6$-$H_4)_2SiO]$ (102); $ClSi(CH_3)_2$—[—$OSi(CH_3)_2$—$]_3Cl$ (121); $ClSi(CH_3)_2$—[—$OSi(CH_3)_2$—$]_4$-Cl, $ClSi(CH_3)_2[$—$OSi(CH_3)_2$—$]_5Cl$ (121); $(CH_3SiO_{1.5})_x$ (114); $(C_2H_5SiO_{1.5})$ (101); [—C_6-$H_4Si(CH_3)(OH)$—$]_x$ (111); Polysiloxane resins (247, 248, 270, 378, 379, 389)

GRIGNARD REAGENTS

CH_3SiCl_3 (99, 104); $(CH_3)_2SiCl_2$ (99, 104, 121); $C_2H_5SiCl_3$ (101); $(CH_3)_3SiCl$ (99, 104); $(C_2H_5)_2SiCl_2$ (101); $C_6H_5SiCl_3$ (100); $(C_2H_5)_3SiCl$ (101); $p\text{-}FC_6H_4SiCl_3$ (100); C_6H_5Si-$(CH_3)Cl_2$ (100, 103); $(p\text{-}FC_6H_4)_2SiCl_2$, $(C_6H_5)_2SiCl_2$, $(C_6H_5)_3SiCl$, $(p\text{-}FC_6H_4)_3SiCl$ (100); $(p\text{-}C_6H_5OC_6H_4)_2SiCl_2$ (102); (—$C_5H_{10}SiCl_2$—$)_x$, (—$C_6H_4SiCl_2O)_x$, (—C_6H_4Si-$(CH_3)Cl$—$)_x$, [—$C_6H_4Si(CH_3)_2$—$]_x$ (111)

INORGANIC SALTS

Polysiloxane resins (378)

INTERCHANGE

$(CH_3)_3SiOSi(CH_3)_2Cl$, $(CH_3)_3SiOSiCl_3$(524)

Specifically, it provides for the preparation of ethylphenyldichlorosilane by successive Grignard action, followed by its hydrolysis under carefully controlled conditions. The polymer was heated at temperatures between 200° and 300° to displace alkyl radicals by oxidation, thus increasing the number of cross linkages.

British Patent 563995 (1944)

In this patent (265) tetrachlorosilane and tetraethoxysilane were converted by the action of a suitable Grignard reagent to $RSiCl_3$ and RSi

$(OC_2H_5)_3$, respectively. These products were hydrolyzed by a mixture of water and ethanol. In the case of the hydrolysis of $RSi(OC_2H_5)_3$, a little hydrochloric acid or oxalic acid served as a suitable catalyst of hydrolysis. Most of the experimental details and comments appear in current United States patents emanating from the same source.

U. S. Patent 2371050 (1945)

Here (113) will be found a description of the preparation and uses of organo-silicon polymers with a silicon content equivalent to at least 20 per cent, based on silicon dioxide. Polymerization of the monomeric silicones was accomplished by heat and dilute hydrochloric acid. Further, by oxidation with or without hydrolysis some of the organic radicals could be burned off with the setting up of cross linkages, silicon-oxygen-silicon.

To make certain that no one silicon atom would combine with too many phenyl groups, the Grignard solution was added to the tetrachloride slowly and with stirring.

The products from alkyl-substituted silanes at one comparable stage were flexible and rubbery, while at the same point of development those from the aromatic diphenyloxosilane were hard and somewhat brittle.

This was what might be called Dr. Hyde's basic patent. Expecially his unique manner of setting up cross linkages by oxidation is commended to the reader. This is the type of reaction which, if kept under control, leads to the setting up of cross links as mentioned in the patent to an extent varying with the amount of ethyl groups, for instance, which have been introduced. Air was bubbled through the material while the latter was kept at a temperature between 200° and 300°. The presence of acetaldehyde in the gases evolved indicated the destruction of ethyl radicals. These transformations were quite naturally accompanied by increases in viscosity. Treatment with nitric acid removed some each of both aryl and alkyl radicals. Applications are also discussed.

U. S. Patent 2375998 (1945)

This work (369) covered the preparation of a conventional silicone by the hydrolysis of polychloro- or polyethoxysilanes. Organic radicals were also attached to the silicones. These polymers were adapted to use as molding powders.

U. S. Patent 2377689 (1945)

This invention (343) relates "to dielectric liquids for electrical apparatus" and its "primary object is to provide a new dielectric liquid". Another object was the working out of improved methods for the insulation of electrical elements and an "apparatus" including a liquid silicone or organo

siloxane. For these purposes various polymerized silicones were prepared and their properties studied.

Thus in Example 5, a co-polymer was prepared consisting of two molar parts of dimethyloxosilane and one of ethylsesquioxosilane. This polymer was a liquid having a viscosity of 54.8 centistokes at 25.0°C. Detailed electrical properties are listed in the patent.

U. S. Patent 2384384 (1945)

This patent (122) covers "the preparation and use of liquids having lubricating properties and specifically characterized by high resistance to oxidation, little change in viscosity with temperature and low pour point . . ." in other words, additional polymers of the silicone family with these properties.

The patent covers the preparation of dimethyloxosilane by the action of "nascent" methylmagnesium chloride on tetraethoxysilane. The method had been satisfactorily reported in chemical literature on numerous occasions by other investigators and was here applied to practical use. Thus dimethyldiethoxysilane was produced and hydrolyzed with water; heat and a catalyst promoted a polymerization reaction and an increase in viscosity. McGregor preferred a mixture of equal parts of 95 per cent ethanol and dilute hydrochloric acid.

It is stated that low polymers, that is, up to about eight silicon atoms per molecule, are really heterocyclic polysiloxanes. Higher polymers were believed to be linear.

U. S. Patent 2386452 (1945)

Fleming (126), assigning to Corning Glass Works, has covered a unique method of preparing "organo silicon compounds" using lithium. For example, "methyllithium was prepared by reacting lithium and methyl chloride in diethyl ether." This solution was then added, with stirring, to an ice-cold solution of tetrachlorosilane in absolute ether. Silicon ethers were prepared by treating the completed reaction mixture with ethanol. Ethyllithium, phenyllithium and various substituted phenyllithiums were also used to advantage. Phenyltriethoxysilane was prepared by the interaction, in one stage, of tetraethoxysilane, lithium and chlorobenzene. For breadth of scope and interest attached to the reactions themselves, this patent ranks high.

U. S. Patent 2386466 (1945)

This patent of J. F. Hyde (372) described again the formation of ethylphenyldichlorosilane by the successive action of ethylmagnesium bromide and phenylmagnesium bromide on tetrachlorosilane. Hydrolysis and polymerization of the product followed.

U. S. Patent 2386467 (1945)

The polymer of the type described here (123) seems to be a corollary of the preceding ones. Tetrachlorosilane was used, however, instead of the more expensive tetraethoxysilane. Again the additional polymerization was brought about by oxidizing alkyl side chains, with the setting up of silicon-oxygen cross linkages and the release of acetaldehyde.

U. S. Patent 2386488 (1945)

In this patent (124), trimethylethoxysilane reacted with "a phosphorus halide", specifically phosphorus pentachloride, to form trimethylchlorosilane. Trimethylethoxysilane was prepared by continued action of a Grignard reagent on tetraethoxysilane.

U. S. Patent 2389802 (1945)

The most interesting and striking point about this patent (249) is the fact that stabilizers investigated were remarkably similar in structure to many of the antioxidants used in rubber and in other polymer compounding. Surely this point should catalyze some generalizations as to the nature of stabilization and the inhibition of oxidation, and possibly the evolution of some common mechanism to explain the action of these inhibitors themselves.

Table 2 proved interesting as well. Methyltrihydroxysilane would lend itself most easily to the formation of cross linkages and therefore to the hardening of the plastic mass. Hence an increase in content of methyltrihydroxysilane, or as expressed, in monomethylsilicon, should result in an increase of tendency toward gelation.

U. S. Patents 2389803, 2389804, 2389805, 2389806 and 2389807 (1945)

McGregor and Warrick followed this investigation with another (254) covering further work on stabilizers. The third in this series (250) listed such stabilizers as phenols and alkyl substitution products, for instance 3-methylcatechol and *t*-butylcatechol. The work was continued under the other consecutively numbered patents (251, 252, 253).

U. S. Patent 2397727 (1946)

This patent (374), dated April 2, 1946, covers a unique method for the formation of mixed polysiloxanes: by the interaction of two relatively simple polysiloxanes, more complex polymers were produced. For instance, polymerized dimethyloxosilane and polymerized ethylphenyloxosilane were heated at 250° in air; and from the products resins were obtained. A mixture of dimethyloxosilane and 1,3-diphenyl-1,1,3,3-tetramethyldisiloxane was also used (Example 4).

U. S. Patent 2405988 (1946)

Compounds of the type $R_n Si(OOCR')_{4-n}$ (518) were prepared, where R and R′ are hydrocarbon radicals. The method involved heating the organosilicon halide with an excess of a metallic salt of some dicarboxylic acid at 60° to 120° for 10 to 20 hours with some diluent, as for instance petroleum ether or toluene. Among the compounds thus prepared were $CH_3 COOSi(OC_{12}H_{25})_3$ and $CH_3 COOSi(OC_{18}H_{37})_3$.

U. S. Patent 2410346 (1946)

Additional data are included here (384) on the hydrolysis of chlorosilanes with the ultimate purpose of preparing lubricants.

British Patents 571725 (1945), 574653 (1946) and 579408 (1946)

Corning Glass Co. has patented in Great Britain various reactions using the Grignard reagent (507) and organic compounds of lithium (508) for the preparation of organic compounds of silicon. Many of these were hydrolyzed (507, 508, 509).

U. S. Patents 2413049 (1946) and 2413050 (1946)

Corning Glass Co. here describes the preparation of a wide range of compounds of the type $RSiCl_3$. In the first patent (519) $CH_3 SiCl_3$ and $(CH_3)_2 SiCl_2$ and in the second (520) $C_{12}H_{25}SiCl_3$, $C_{14}H_{29}SiCl_3$ and $C_{18}H_{37} SiCl_3$ are given.

U. S. Patent 2413389 (1947)

Dow Chemical Co. has covered (515) the preparation of polysiloxanes with two radicals attached to each silicon and with alkoxyl groups at the ends of the chains. These products were prepared by alkaline hydrolysis of dialykyldialkoxysilanes.

British Patents 583875 (1947) and 583878 (1947)

In these two British patents, Corning Glass Co. (516, 517) has described methods of altering the viscosity of various silicones by treatment with alkali oxides, alkaline earths or quarternary ammonium hydroxides.

British Patent 585400 (1947)

Hexasubstituted disiloxanes were prepared (525) by hydrolysis and condensation of tetraalkylchlorosilanes, and dialkyldichlorosilanes in the presence or absence of organic solvents and hydrochloric acid. The products were non-resinous liquids.

In summarizing the contributions of Corning Glass and related laboratories, attention should be called to the methods used in setting up cross

linkages in silicon polymers. By heating with oxygen organic radicals were burned off; as a result, polysiloxane linkages were created (113). Methods of preparation comprised the use of the Grignard reagent in most cases (113, 122, 123, 343) and the newer use of lithium (126). Phosphorus pentachloride, reacting with a silicon-ethoxyl linkage, converted it to silicon-chlorine (124). The British patents listed here describe procedures of preparation and hydrolysis roughly parallel to those covered elsewhere. Finally, considerable attention has been paid to stabilizers (249, 250, 251, 252, 253, 254).

Table 12. Compounds Prepared at Moderate Temperatures, Methods Covered by Corning Glass and Allied Patents.

WATER

$CH_3Si(OH)_3$ (122, 123, 126, 507, 508); $(CH_3)_2Si(OH)_2$ (113, 123, 126, 507, 508); $(CH_3)_2$-SiO (122, 123, 126); $(CH_3)_3SiOH$ (126); $C_6H_5Si(C_2H_5)(OH)_2$, $C_6H_5Si(C_2H_5)O$ (113, 123); $[(CH_3)_2NC_6H_4]_3SiOH$ (126); $[(CH_3)_2SiO]_3$ (122, 507); $[C_6H_5Si(C_2H_5)O]_3$ (113, 123); Polymers (113, 122, 123, 265, 343, 369, 372, 384, 441, 507)

LITHIUM ALKYLS

CH_3SiCl_3 (126, 369); $(CH_3)_2SiCl_2$ (126, 508); $(CH_3)_3SiCl$ (126); $(C_2H_5)_2SiCl_2$ (508); $C_6H_5SiCl_3$ (508); $CH_3OC_6H_3(Br)SiCl_3$, $C_6H_5CH_2SiCl_3$ (126, 508); $C_6H_5Si(CH_3)Cl_2$ (126); $C_6H_5Si(C_2H_5)Cl_2$ (508); $C_6H_5Si(CH_3)(OC_2H_5)_2$ (126); $(C_6H_5)_2SiCl_2$ (126, 508); $H_2NC_6H_4Si(OC_2H_5)_3$ (126); $C_6H_5Si(OC_2H_5)_3$ (265); p-$CH_3C_6H_4Si(OC_2H_5)_3$, $(CH_3)_2$-$C_6H_3Si(OC_2H_5)_3$, $(C_6H_5)_3SiCl$, p-$C_6H_5C_6H_4Si(OC_2H_5)_3$, $(p$-$HOCH_2C_6H_4)_2Si(OC_2H_5)_2$, $[p$-$(CH_3)_2NC_6H_4]_3SiCl$ (126)

GRIGNARD REAGENTS

CH_3SiCl_3, $(CH_3)_2SiCl_2$ (507, 519); $C_2H_5SiCl_3$ (113, 123); $(C_2H_5)_2SiCl_2$ (507); $(CH_3)_2Si$-$(OC_2H_5)_2$ (122, 123); $(CH_3)_3SiOC_2H_5$ (124); $CH_3Si(OC_2H_5)_3$ (122, 369); $C_6H_5Si(C_2H_5)Cl_2$ (113, 123, 372, 441); $(C_4H_9)_2SiCl_2$, $(C_5H_{11})_2SiCl_2$ (507); $C_{12}H_{25}SiCl_3$, $C_{14}H_{29}SiCl_3$, $C_{18}H_{37}SiCl_3$ (520)

PHOSPHORUS PENTACHLORIDE

$(CH_3)_3SiCl$ (124)

STABILIZERS

Polymers (249, 250, 251, 252, 253, 254)

INTERACTION

Polymers (374)

SODIUM ACETATE

$CH_3 COOSi(OC_{12}H_{25})_3$, $CH_3COOSi(OC_{18}H_{37})_3$ (518)

MISCELLANEOUS GROUPS

From a purely chronological point of view, the first patents of the third group to become effective were taken out by E. I. du Pont de Nemours and Co. in 1941.

U. S. Patent 2238669 (1941)

The procedure (223) followed the pattern of Kipping's many researches in using a modified Wurtz-Fittig reaction for the preparation of alkyl-substituted silanes:

Example 1. $C_6H_5Cl + (C_6H_5)_3SiF + 2Na \rightarrow NaCl + NaF + (C_6H_5)_4Si$.

The proportions approximated theoretical ratios.

Example 2. $SiF_4 + 4C_6H_5Cl + 8Na \rightarrow 4NaCl + 4NaF + (C_6H_5)_4Si$.

The second method gave a yield of 23 per cent. It should be noted that the apparatus used in Example 2 was swept out thoroughly with nitrogen free from oxygen before using; this later become common procedure. It should also be noted that the solvent was inert to alkalies and alkali alkyls or aryls, and that there were no substituents in the radicals which might have given rise to side reactions.

British Patent 542166 (1941)

In the words of this patent (364), compounds were prepared of the general formula $(CHR=CR'-COO)_xM(R'')_y$, where R, R' and R'' may be hydrogen or a hydrocarbon radical. R'' may be halogen. The sum of x and y must equal four. M may be silicon or tin, the latter tetravalent. This is a most interesting type of reaction because of the normal possibility of polymerization through hydrolysis and subsequent loss of water on the silicon end of the molecule, together with normal polymerization on the acrylic end. Indeed the two may take place simultaneously and the acrylic portion may co-polymerize with such other monomers as styrene. The possibilities here seem endless.

U. S. Patent 2397287 (1946)

Almost as a sequel to the above, the Polaroid Corporation (456) has covered the reaction between tetraethoxysilane and methacrylic acid by which there was obtained a quantitiative yield of ethyl alcohol and triethoxysilicyl methacrylate. This was done at 760 mm, with pyrogallol as inhibitor of polymerization. The product polymerized with heat and benzoyl peroxide. Co-polymers were prepared with methacrylates, vinyl ethers, vinyl ketones, styrene, vinylnaphthalene and vinylfuran. In addition, methacrylate co-polymers were hardened with methacrylic acid, acrylic acid or allyl methacrylate.

British Patent 542655 (1942)

This is a Thomson-Houston patent (440). It covers patentable variations of (1) a method for the preparation of a methyl silicone condensation product by hydrolysis of the halide; (2) a method for the further condensation of this product at higher temperatures; and (3) a liquid coating composition, as well as (4) synthetic resins.

British Patent 544143 (1942)

Chlorination of diphenyldichlorosilane (366) provided a method for introducing three chlorines into each aromatic ring. The resulting product

was practically non-flammable. In addition, the electrical conductivity ranged from 10^{-9} reciprocal ohms per cc at 320° to 10^{-13} at room temperatures. Hydrolysis and the controlled change of properties of the hydrolyzate on heating were carried out much as has been described elsewhere. Di-*p*-fluorophenyldichlorosilane was prepared through *p*-fluorophenylmagnesium bromide. Iodination of diphenyldichlorosilane by means of iodine and iodine pentoxide formed diiodophenyldichlorosilane. Practical uses of halogenated silicones were discussed, as well as their preparation from the halides just described.

British Patent 548911 (1942)

It will be noted that the preparation (105) of methylphenyldichlorosilane was here brought about by the interaction of methylmagnesium bromide, phenylmagnesium bromide and tetrachlorosilane in the molar proportions of 2.19/1.35/1.90. The ratio of $CH_3/C_6H_5/Si$ in the final, water-hydrolyzed product was 0.85/1.26/1.90. A much higher proportion of phenyl than methyl had obviously reacted.

Hydrolysis was brought about by pouring the ether solution of the dichloro compound over cracked ice. During condensation and consequent loss of water forming the silicon-oxygen-silicon bonds, toluene was added to facilitate distillation of this water.

British Patent 548912 (1942)

From the standpoint of organic syntheses, it will be noted here (106) that *p*-bromodiphenylether was allowed to react with magnesium; then 0.401 mole of the resulting Grignard reagent was reacted with 0.234 mole of tetrachlorosilane. The theoretical ratio would have been 0.401/0.200. A small amount of *p*-phenoxyphenyltrichlorosilane was formed along with di-*p*-phenoxyphenyldichlorosilane. As before, hydrolysis was accomplished by pouring over cracked ice. Condensation to the etheric polymer was brought about by heating at 110° for four hours. Polymerization continued from this point giving higher polymers, but temperatures of from 150° to 225° were necessary. Results on one run specified in the patent gave a radical/Si ratio of 1.09/1.00, which would indicate a fairly high percentage of $RSiCl_3$ in the reaction mixture as against R_2SiCl_2. However, even this would give a fair amount of cross linking.

British Patent 549081 (1942)

Emphasis was placed in this patent (107) on methods of condensation as applied to the conversion of dihydroxysilanes and trihydroxysilanes to complex silicones. A rather imposing list of dehydrating agents will be found here. Triethyl orthoborate effected polymerization through dehy-

dration at 190° in ten minutes. Antimony pentachloride and sulfuric acid, separately, were effective at room temperatures, while ethylene diamine "formed a solid polymer when heated for one hour at 120° C."

British Patent 551649 (1943)

The products covered here (109) were oxosilanes, *i.e.*, polymers with ethyl radicals. The ratio of ethyl to silicon varied between 0.5/1.0 and 1.5/1.0. There does not seem to be much that is different in type in this patent from some others. The patentable material is new, however, and the field is well covered.

British Patent 552640 (1943)

The procedure outlined in this patent (110) was varied so that silicon-carbon-silicon linkages could be obtained in the final polymer. For instance, the di-Grignard reagent was prepared from *p*-dibromobenzene, and this product, in absolute ether solution, was allowed to react with tetrachlorosilane. A mixture of isomeric dichloropentanes was also found satisfactory in place of the *p*-dibromobenzene. To the semi-polymerized product resulting from the action of p-$C_6H_4(MgBr)_2$ on tetrachlorosilane, methylmagnesium bromide was added, introducing a methyl group in the chain.

British Patent 590654 (1947)

The British Thomson-Houston Co.[647] (1947) has covered improved yields of silicon compounds comprising the treatment of powdered silicon with alkyl halides or alcohols.

U. S. Patent 2413582 (1946)

This patent, assigned to Montclair Research Corporation and Ellis-Foster Co. (521), covered the preparation of organic compounds of silicon synthesized through lithium organic reagents.

U. S. Patent 2388161 (1945)

The American Cyanamid Co. (125) has covered the preparation of tetraallylsilane for possible use in polymers. The unsaturation of the allyl groups is of especial use and advantage here.

U. S. Patents 2030736 (1936), 2030737 (1936), 2030738 (1936) and 2030739 (1936)

These three patents, issued to the North American Rayon Corp., (541, 542, 543, 575) cover various items, such as the spinning together of viscose or cuprammonium cellulose with compounds such as $RSiH_2$—SiH_2R' (541)

and the preparation of organic compounds of silicon and their uses (542, 543, 575).

U. S. Patent 2407181 (1946)

A most interesting type of wax-like polymer has recently been reported by the du Pont laboratories (619). This polymer results from the interaction, in a pressure reactor, of "78 parts of cyclohexane, 30 parts of silicon tetrachloride, one part of hexachloroethane and one part of mercuric chloride." Ethylene was then pumped in and the mixture heated until the final temperature had reached 275° and the pressure 900 atmospheres. Five examples listed in the patent covered variations of this procedure. Another paragraph lists the catalysts covered and the silicon compounds which could be expected to react.

Apparently the products resulting here were different from the ordinary run of silicon organic polymers. They were more like polymerized olefins in nature, *i.e.*, waxy and greasy. There was a difference, however, in contrast to the usual polymerized olefin.

Table 13.   Compounds Prepared at Moderate Temperatures, Methods Covered by Other Patents.

WATER

$CH_3Si(OH)_3$, $(CH_3)_2Si(OH)_2$ (107); $C_2H_5Si(OH)_3$ (109); $(CH_3)_3SiOH$ (107); $(C_2H_5)_2Si(OH)_2$, $(C_2H_5)_3SiOH$ (109); $C_6H_5Si(CH_3)(OH)_2$ (105, 366); $(p\text{-}C_6H_5OC_6H_4)_2Si(OH)_2$, $p\text{-}C_6H_5OC_6H_4Si(OH)_3$ (106); $(C_6H_5)_2Si(OH)_2$, $(p\text{-}FC_6H_4)_2Si(OH)_2$, $(Cl_3C_6H_2)_2Si(OH)_2$ (366); $HOSi(C_6H_5)(CH_3)OSi(C_6H_5)(CH_3)OH$, $HOSi(C_6H_5)(CH_3)\text{—}[\text{—}OSi(C_6H_5)\cdot(CH_3)\text{—}]_2OH$, $[C_6H_5Si(CH_3)O]_3$ (105); $HOSi(C_6H_2Cl_3)_2OSi(C_6H_2Cl_3)_2OH$ (366); $HOSi\text{-}(C_6H_4OC_6H_5)_2OSi(C_6H_4OC_6H_5)_2OH$ (106); $HOSi(C_6H_2Cl_3)\text{—}[\text{—}OSi(C_6H_2Cl_3)_2]_2\text{—}OH$ (366); $[(p\text{-}C_6H_5OC_6H_4)_2SiO]_3$, $HOSi(C_6H_4OC_6H_5)_2\text{—}[\text{—}OSi(C_6H_4OC_6H_5)_2\text{—}]_2OH$ (106); $[(CH_3)_2SiO]_x$ (107, 440); $[\text{—}C_6H_4Si(CH_3)(OH)\text{—}]_x$ (110)

GRIGNARD REAGENTS

$C_2H_5SiCl_3$, $(C_2H_5)_2SiCl_2$, $(C_2H_5)_3SiCl$ (109); $C_6H_5SiCl_3$ (366); $C_6H_5Si(CH_3)Cl_2$ (105, 366); $(CH_2\text{=}CHCH_2)_4Si$ (125); $p\text{-}C_6H_5OC_6H_4SiCl_3$ (106); $(C_6H_5)_2SiCl_2$, $(p\text{-}FC_6H_4)_2SiCl_2$ (366); $(p\text{-}C_6H_5OC_6H_4)_2SiCl_2$ (106); $(\text{—}C_6H_4SiCl_2\text{—})_x$, $[\text{—}C_6H_4Si(CH_3)Cl\text{—}]_x$, $[\text{—}C_6H_4Si(C_5H_{10}\text{—})\text{—}]_x$ (110)

SODIUM AND CHLOROBENZENE

$Si(C_6H_5)_4$ (223)

POTASSIUM METHACRYLATE

$Si[OOCC(CH_3)\text{=}CH_2]_4$ (364)

HALOGENS

$(Cl_4C_6H)Si(CH_3)Cl_2$, $(Cl_3C_6H_2)_2SiCl_2$, $(IC_6H_4)_2SiCl_2$ (366)

METHACRYLIC ACID

$CH_2\text{=}C(CH_3)COOSi(OC_2H_5)_3$ (456)

OLEFINS

Waxy polymers (619)

Chapter 6

Organic Compounds of Silicon Prepared at Higher Temperatures

In Chapter 4 one of the chief reactants in the preparation of substituted silanes was the Grignard reagent. This chapter will discuss syntheses involving organic halides and alloys of silicon, the net results of which are that silicon is found in a stable chemical compound, linked to both carbon and halogen, as in Chapter 4. The chief difference, however, between the Grignard type of reaction and those involving silicon alloys is that, whereas the former take place in the presence of low-boiling solvents and the product is generally ether-soluble, the interaction of organic halides and the silicon-copper or other alloy occurs at much higher temperatures and between the solid and the vapor states. At least the reactants are introduced as solid and vapor. The products are generally distillable from the reaction chamber.

The first recorded work on the action of organic halides on elemental silicon appeared in 1945 (152). A silicon-copper alloy, in molar ratio 9:1, was treated with the vapors of methyl chloride at high temperatures, forming methyltrichlorosilane and dimethyldichlorosilane. The reaction was found quite satisfactory also for methyl bromide, ethyl chloride, ethyl bromide, chlorobenzene and bromobenzene.

Under favorable conditions, some 70 per cent of the yield was R_2SiX_2, with smaller amounts of R_3SiX and $RSiX_3$; there were even smaller percentages of SiR_4 and SiX_4. If the circumstances of the reaction were such as to favor pyrolysis, organic radicals decomposed and derivatives such as $RSiHX_2$ were formed. Possible reactions can then be summarized in the equations given by the author of the paper as follows:

$$2RX + Si \rightarrow R_2SiX_2$$
$$3RX + Si \rightarrow RSiX_3 + R_2$$
$$R_2 \rightarrow \text{decomposition}$$
$$3RX + Si \rightarrow R_3SiX + X_2$$
$$2X_2 + Si \rightarrow SiX_4$$
$$4RX + 2Si \rightarrow SiX_4 + SiR_4$$
$$2RX + Si \rightarrow RSiHX_2 + H_2 + C.$$
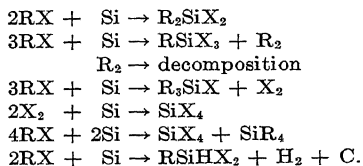
Hurd and Rochow (351) continued this study, presenting data and mechanisms for the function of copper in the interaction of silicon and an

organic halide at high temperatures. This subject was later summarized by Rochow in 1946 (349):

$$2Cu + CH_3Cl \rightarrow CuCl + CuCH_3 \text{ (at } 250°)$$
$$Si + CuCl \rightarrow Cu + (SiCl) \text{ (activated Si)}$$
$$(SiCl) + CH_3 \rightarrow (CH_3SiCl) \text{ (activated Si)}$$
$$(SiCl) + CuCH_3 \rightarrow (CH_3SiCl) + Cu$$
$$(SiCl) + CuCl \rightarrow (SiCl_2) + Cu$$
$$(CH_3SiCl) + CuCl \rightarrow (CH_3SiCl_2) + Cu$$
$$(CH_3SiCl_2) + CuCH_3 \rightarrow (CH_3)_2SiCl_2 + Cu.$$
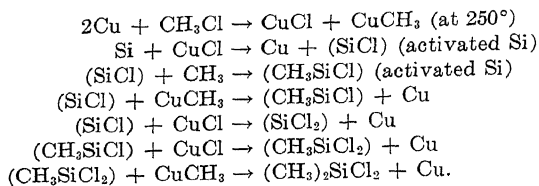
A contribution by D. T. Hurd (354) covered vapor-phase reactions by means of which chlorosilanes were alkylated by alkyl halides in the presence of finely divided metal such as aluminum or zinc, at temperatures ranging from 300° to 500°. Hydrolysis of the products resulting from the interaction of tetrachlorosilane and methyl chloride gave a resinous product resembling polymerized silicones. Methyltrichlorosilane and methyl chloride formed trimethylchlorosilane (21 per cent), dimethyldichlorosilane (11 per cent) and a trace of methyldichlorosilane at 450°. At 350° these figures were changed somewhat, and at 400° a certain amount of tetramethylsilane was isolated. Dimethylchlorosilane and methyl chloride gave a 30 per cent yield of trimethylchlorosilane, and a mixture of dimethyldichlorosilane and ethyl chloride formed dimethylethylchlorosilane Dimethyldibromosilane and methyl bromide produced trimethylbromosilane.

Hydrogenation in general resulted in replacement of chlorine by hydrogen, whether in tetrachlorosilane or some of the methyl derivatives.

Hurd believed that the reactions could be expressed as:

$$2Al + 3CH_3Cl \rightarrow CH_3AlCl_2 + (CH_3)_2AlCl$$
$$(CH_3)_2AlCl + 2(CH_3)_2SiCl_2 \rightarrow 2(CH_3)_3SiCl + AlCl_3$$
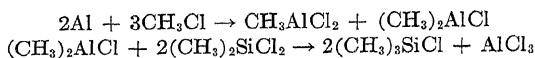
The action of these compounds at high temperatures is logical evidence, according to Hurd, for by Gilman's Rule; if aluminum passes radicals to silicon in exchange for chlorine, then it would be expected that aluminum metal would displace silicon from its compounds with radicals:

$$(CH_3)_2SiCl_2 + Al \rightarrow (CH_3)AlCl + (SiCl)$$
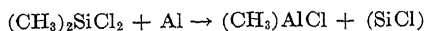
Radical interchange was also observed.

Rochow and Gilliam (356) have reported the action of chlorobenzene on a silicon-copper alloy (4/1) in the presence of dry hydrogen chloride. At 550° this reaction resulted in the production of 12.7 per cent of phenyltrichlorosilane, based on the weight of chlorobenzene used. The net result of this investigation was the conclusion that silver is the best catalyst for this purpose, with copper in second place. Phenyltrichlorosilane and diphenyldichlorosilane were the products, formed at 400°. Phenyldichlorosilane (446) was also reported.

Hurd has also prepared (357) vinylchlorosilanes and allylchlorosilanes by the high-temperature action of the proper alkylene chloride, *e.g.*, vinyl chloride, allyl chloride, on silicon-copper alloys. Thus were prepared compounds of the general formulas $(CH_2=CH)_xSiCl_{4-x}$ and $(CH_2=CHCH_2)_xSiCl_{4-x}$. The preparation of vinyltrichlorosilane was checked by preparing ethyltrichlorosilane, chlorinating the ethyl group and then abstracting HCl.

The silicon-copper alloy, 9/1, in a "Pyrex" tube was treated with a stream of allyl chloride vapors. It was necessary to dilute the latter with nitrogen because pure allyl chloride reacted so fast and so exothermally that the temperature rose to 500° to 600°, thereby limiting yields and initiating decomposition. The reaction was successful at 250°. About 60 per cent of the products were of the desired type, the remainder being chlorides of silicon without the allyl group. Allyltrichlorosilane, diallyldichlorosilane and triallylchlorosilane were isolated. Allyltrichlorosilane reacts with methylmagnesium bromide to form allyltrimethylsilane. Yields of the corresponding vinyl compounds were small.

Alkylenechlorosilanes hydrolyzed in ether and ice with no loss of unsaturation. Polysiloxanes thus formed polymerized under the influence of the usual catalysts, such as benzoyl peroxide.

R. N. Meals (362) prepared ethyldichlorosilane by the action of ethyl chloride on a silicon-copper alloy at 300°.

Gilliam, Meals and Sauer (435) have reported the preparation of methyltribromosilane, dimethyldibromosilane and trimethylbromosilane by the action, at high temperatures, of methyl bromide on a silicon-copper alloy, which was sintered in the atomic ratio of 4/1. It was noted that an impurity or by-product resulted, which was assumed to be tribromosilane.

In 1945 a patent was granted and assigned to General Electric Co., to cover this newer type of synthesis (U. S. 2380995) (153). As Dr. Rochow has stated, silicon is a metalloid rather than a metal, and this fact may account for the high temperatures (200°–500°, "or more") necessary to effect this type of reaction. On the whole however, the direct reaction seems to be a very good method for the preparation of methyltrichlorosilanes in good yields. Relative yields of the various products were found to vary with the temperatures used.

The above patent was followed by others from the same source (154, 155, 156, 157, 158, 159, 160, 162). In U. S. Patent 2380999 (157) better control was obtained by the use of an inert gas such as nitrogen to dilute the organic halide. In Example 1 of this patent a yield of 73.5 per cent of dimethyldichlorosilane was reported, as well as 9 per cent of methyltrichlorosilane and 6 per cent of trimethylchlorosilane.

Patnode and Schiesser's U. S. Patent 2381000 (158), assigned to General Electric Co., covered a synthesis of organic compounds of silicon by the

simultaneous action of the silicon-copper contact mass on two ends of an alpha-omega dihalide, for instance, ethylene dichloride. A mixture of dry, oxygen-free nitrogen and ethylene dichloride was passed over the contact mass at a temperature of 370° to 380°. Some 70 per cent of the organic halide either reacted or was recoverable; 1,2-di-trichlorosilylethane was formed. Carbon tetrachloride (159) formed tetrachloroethylene and hexachlorodisilane. Cyclic alkylsilanes with two chlorine atoms still attached to each silicon (160) were also prepared.

U. S. Patent 2379821 (161) outlined a process for the preparation of "organic silicon compounds" by the interaction, *e.g.*, in Example 1, of benzene and trichlorosilane at 750° to 770°. The catalyst was fused quartz and small pieces of clay plate. Phenyltrichlorosilane was the chief product, although yields were not specified.

Obviously the mechanism of this type of reaction is radically different from that which makes use of the silicon-copper alloy. In the reaction which formed the basis of the above-mentioned invention there must of necessity have been dehydrogenation:

$$C_6H_6 + HSiCl_3 \rightarrow H_2 + C_6H_5SiCl_3$$
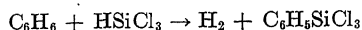
The preparation of the same compound was claimed by the passage of vapors of benzene and tetrachlorosilane through a quartz tube heated to redness. This seems to be an example of the abstraction of a hydrohalogen acid, apparently by the catalytic action of the quartz:

$$C_6H_6 + SiCl_4 \rightarrow HCl + C_6H_5SiCl_3$$
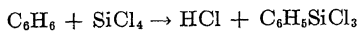
The clay catalyst also sufficed for the preparation of organic compounds of silicon containing chlorine when the starting materials were olefins and either trichlorosilane or tetrachlorosilane. Formulas for these products were not indicated. Also, from butane there was obtained a fraction which corresponded in formula to butyltrichlorosilane.

It is well known from work, both published and unpublished, that the aluminum chloride or Friedel-Crafts type of catalyst will not operate satisfactorily in either of these reactions. Consequently the attainment of even small yields should be noted with interest and the literature closely watched for further developments in this field.

C. E. Waring (352) has postulated the mechanism for thermal decomposition of tetraethylsilane and tetrapropylsilane as follows:

$$Si(C_2H_5)_4 \rightarrow Si + 4C_2H_5$$
$$Si(C_2H_5)_4 \rightarrow Si(C_2H_5)_3 + C_2H_5 \text{ (slow)}$$
$$Si(C_2H_5)_3 \rightarrow Si + 3C_2H_5 \text{ (fast)}$$
$$C_2H_5 \rightarrow C_2H_4 + H$$
$$2H \rightarrow H_2 \text{ (fast)}$$
$$C_2H_4 \rightarrow CH_4 + C \text{ (slow)}$$

$$Si(C_3H_7)_4 \rightarrow Si + 4C_3H_7$$
$$Si(C_3H_7)_4 \rightarrow Si(C_3H_7) + C_3H_7 \text{ (slow)}$$
$$Si(C_3H_7)_3 \rightarrow Si + 3C_3H_7 \text{ (fast)}$$
$$C_3H_7 \rightarrow C_3H_6 + H$$
$$2H \rightarrow H_2 \text{ (fast)}$$
$$C_3H_6 + 2H \rightarrow C_2H_4 + CH_4$$
$$C_2H_4 \rightarrow CH_4 + C \text{ (slow)}$$
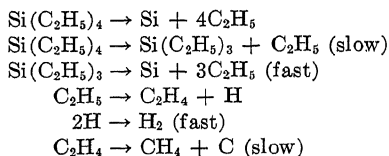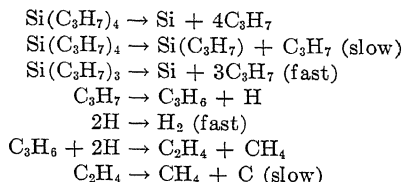
D. T. Hurd (460), assigning to the General Electric Co., has covered the substitution of alkyl radicals for halogens attached to silicon at high temperatures. In the original substituted silane, R_xSiCl_{4-x}, x must be at least 1. Aluminum or zinc was found satisfactory as the catalyst. Thus a 1:1 molar mixture of dimethyldichlorosilane and methyl chloride reacted at 350° to give a 30 per cent yield of trimethylchlorosilane. Methyltrichlorosilane reacted to form trimethylchlorosilane (6 per cent), and dimethyldichlorosilane (4.5 per cent also at 350°). Stepping up the latter temperature to 450° increased the yields to 11 and 21 per cent, respectively. There was also formed 3 to 4 per cent of CH_3SiHCl_2. In 2:1 molar ratio, dimethyldibromosilane and methyl bromide reacted over aluminum at 350° forming trimethylbromosilane; dimethyldibromosilane and ethyl chloride gave dimethylethylchlorosilane. Methyl chloride over zinc at 375° formed trimethylchlorosilane in 30 per cent yield.

General Electric Co.[668] has reported in U. S. Patent 2420912 (1947) passage of allyl chloride over the usual 9:1 silicon-copper alloy at 230°–300° to form allyldichlorosilane. Allyltrichlorosilane and diallyldichlorosilane were formed at the same time. Allyltrichlorosilane reacted with methylmagnesium bromide to form allylmethyldichlorosilane. Diallyldichlorosilane easily polymerized above 150°. When ethyltrichlorosilane was chlorinated, then treated with quinoline at 200°, vinyltrichlorosilane was formed. In similar manner ethylmethyldichlorosilane gave methylvinyldichlorosilane and diethyldichlorosilane gave divinyldichlorosilane. Passage of vinyl chloride over the silicon copper alloy at 300°–500° caused the formation of vinyltrichlorosilane and divinyldichlorosilane.

The Plax Corporation (458) has patented the preparation of alkylhalogenated silanes by interaction of tetrachlorosilane and hydrocarbons at 840° to 960°. Thus were made diphenyldichlorosilane at 840° and at 980° triphenylchlorosilane. At 960°, over iron, methane and tetrachlorosilane reacted to form methyltrichlorosilane.

The American Stove Company (526) has patented the treatment of chlorooxosilanes with two parts by weight of phenol, followed by a gradual increase in temperature to 850°F. HCl came off first at about 400°. Phenoxysilanes boiled away and were collected. Phenoxysilanes were obtained with as many as seven silicon atoms per molecule of the general formula $Si_nO_{n-1}(OC_6H_5)_{2n+2}$.

Nor is British interest wanting. The British Thomson-Houston Co. (612, 613) has patented the preparation of alkylchlorosilanes by the action, at temperatures between 200° and 600°, of alkyl halides on an intimate mixture of silicon and copper. A third patent (614) has covered the method of producing this solid porous contact mass. Copper in the alloy runs between 2 and 45 per cent, the remainder is silicon. The intimate mixture is fired in a reducing atmosphere at temperatures between 700° and 1600° long enough to make the copper catalytically active. Cooling also takes place in a non-oxidizing atmosphere.

The British Thomson-Houston Co. (647) has also covered an improved preparation of compounds such as dimethyldichlorosilane by interaction of alkyl halides and silicon at high temperatures. Under the conditions specified, higher yields are claimed.

To summarize this chapter is to point out first of all that the application of high-temperature syntheses in the organic chemistry of silicon is so new and novel that the possibilities have hardly even been indicated. There is the advantage of operating in the dry way, in absence of possibly dangerous solvents, such as ether. But there would also seem at this early stage to be the disadvantage that the temperatures involved might prevent some desired products even from existing. True, the carbon-silicon bond is unusually stable, but molecular fragments are not necessarily stable at high temperatures, and apparently the reactants must dissociate into some sort of fragments before recombination in the desired form. Free methyls, ethyls, etc., have been prepared, however, by Rice, Paneth and others, and it is not at all surprising that these radicals can now successfully be put through other reactions. By an ingenious combination of methyl chloride and hydrogen, derivatives of silane have been produced with one hydrogen connected to silicon. Dry oxygen-free nitrogen served in most cases as a gas diluent.

Table 14. Compounds Prepared at Higher Temperatures.
WITH SILICON

$HSiCl_3$ (153); CH_3SiCl_3 (153, 458); CH_3SiHCl_2, $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$, $Si(CH_3)_4$ (153); $C_6H_5SiHCl_2$ (446); $C_6H_5SiCl_3$ (153); $(C_6H_5)_2SiCl_2$, $(C_6H_5)_3SiCl$ (153, 458)

WITH SILICON AND COPPER

H_2SiCl_2 (158); $HSiCl_3$ (154, 158); $SiCl_4$ (153, 154, 158); CH_3SiF_3 (153, 154); CH_3SiCl_3 (152, 153, 154, 156, 157, 162); CH_3SiHCl_2 (152, 156); CH_3SiBr_3 (153, 154, 156, 435); CH_3SiI_3 (153, 154); $(CH_3)_2SiF_2$ (153, 154); $(CH_3)_2SiCl_2$ (152, 153, 154, 156, 157, 162); $(CH_3)_2SiBr_2$ (153, 154, 156, 435); $(CH_3)_2SiI_2$ (153, 154); $C_2H_5SiCl_3$ (357) 668; $C_2H_5SiCl_3$ (153, 154); $C_2H_5SiBr_3$ (153, 156); $C_2H_5SiHCl_2$ (362); $C_3H_5SiCl_3$ (357) 668; $(CH_3)_3SiF$ (153, 154); $(CH_3)_3SiCl$ (152, 153, 157, 162); $(CH_3)_3SiBr$ (435); $(CH_3)_3SiI$ (153, 154); $C_3H_7SiCl_3$, $C_3H_7SiBr_3$ (156); $Si(CH_3)_4$ (152); $(C_2H_5)_2SiCl_2$ (153, 154, 158); $(C_2H_5)_2SiBr_2$

Table 14—*Concluded*

(153, 156, 157); $(C_2H_3)_2SiCl_2$ (668); $C_6H_5SiCl_3$ (153, 157, 162, 356); $C_6H_5SiBr_3$ (153); $C_6H_{10}SiCl_2$ (357); $(C_2H_5)_3SiBr$ (153, 156, 157); $(C_3H_7)_2SiCl_2$ (156, 157); $(C_3H_7)_2SiBr_2$ (156); $(C_4H_9)_2SiBr_2$ (161); $C_9H_{15}SiCl$ (357); $(C_3H_7)_3SiCl$ (156, 157); $(C_3H_7)_3SiBr$ (156); $C_{10}H_7SiCl_3$ (161); $(C_6H_5)_2SiCl_2$ (155, 157, 162); $(C_6H_5)_3$ SiBr (153); $Cl_3SiSiCl_3$ (159); $Cl_3SiCH_2SiCl_3$, $Cl_3SiCH_2SiHCl_2$ (158, 160); $Cl_3SiCH_2CH_2SiCl_3$ (158); $(Cl_2SiCH_2)_3$ (158, 160)

WITH ALUMINUM

CH_3SiHCl_2 (460); CH_3SiCl_3 (354); $(CH_3)_2SiCl_2$, $(CH_3)_3SiCl$, $(CH_3)_3SiBr$ (354, 460); $Si(CH_3)_4$ (354); $(CH_3)_2Si(C_2H_5)Cl$ (354, 460)

WITH QUARTZ

$C_6H_5SiCl_3$, $C_{10}H_7SiCl_3$ (161)

Chapter 7

The Uses of Polymerized Oxosilanes

To compile, accurately and efficiently, data on the uses of any type of chemical product and to keep this compilation up to date is a well-nigh hopeless undertaking. This chapter should therefore be read with the understanding that the data herein are presented as of the time of writing and with due allowance for all the changes which time may bring.

Sponsors of Dow Corning products presented data on the general properties and uses of silicones in Fisher Scientific Co.'s "The Laboratory" (274) and later announced production (402, 403).

Simonds, Bigelow and Sherman (272) have summarized information through 1945 by listing the uses of polymerized oxosilanes, or silicones as (1) insulation coating compositions, final polymerization of which sometimes takes place as the material is baked on the wire; (2) sheet insulation by impregnation; (3) protective coatings for glass bulbs, etc., by means of which objects are rendered practically shatterproof; (4) conductive points, for instance graphite in silicone paints with any degree of electrical conductivity; and (5) sealing compositions, metal to glass, vacuum-tight. These products range from viscous fluids to resins. All withstand high temperatures and the liquids are pourable at temperatures far below zero.

R. W. Kolderman (393) of Dow Corning Corporation has also written a survey of silicones and their properties.

Rochow and Norton (246) have presented a survey of silico organic chemistry as it bears on polymerized silicones, dated 1946, while R. R. McGregor (377) has listed additional data along the same line.

A group of General Electric patents (100, 101, 102, 103) claimed liquid coating compounds consisting of silicone polymers mostly chlorinated in some volatile solvent. The silicon compounds were incompletely polymerized at the moment of compounding of the coating mixture. Polymerization was brought to completion after application. In addition, these patents covered articles of manufacture coated with the polymers, including electrical conductors.

Reference 100 also covered the non-flammable properties of those chlorinated silicones with at least three chlorine atoms per molecule attached to aromatic nuclear carbons.

The British Thomson-Houston Co. claimed polymerized silicon compounds of the silicone type, for use as coating and impregnating materials (105), as binders with inorganic fillers for electrical insulation to resist temperatures higher than would be withstood by ordinary fillers (106) and insulating materials in general (107, 109, 110).

Electrical insulation was also covered by General Electric's U. S. Patents 2352974 (111) dated 1944, and 2408822 (388) in 1946. The latter of these covered electrical constructions, coated with hydrolyzed silicones.

Corning Glass has U. S. Patents 2386466 (372) and 2377689 (343), as well as British Patent 561226 (644), which also cover insulation materials. Many practical applications of silicones were pointed out in other Dow Corning publications (429, 430) including that of insulating coverings.

Westinghouse Electric and Manufacturing Co. patented a "Semiconducting Composition" as U. S. Patent 2377600 (1945) (345).

This patent brought to the fore innumerable questions as to how far investigation has progressed toward determining exactly the influence of constituents of a mixture such as mentioned therein. Anthracite coal and silicone, mixed as described must have some combined influence due perhaps to the nature of the additive compound or compounds which they might form with each other. A more detailed study of the properties of these additive products, of their physical chemistry and of their adsorptive powers would indeed make an interesting assignment.

From insulators, it is but a step to a consideration of coating compositions in general. General Electric (100, 101, 102, 103) has gone beyond the field of insulators in the patents already mentioned.

U. S. Patent 2306222 (108) covered "the production of water-repellant materials by treating solid bodies normally water-non-repellant with a composition comprising an organo-silicon halide. . . . in vapor form thereby to render the said body water-repellant."

Example 1 described the spreading of a thin water-repellant coating over glass by painting the surface with a mixture of methyltrichlorosilane and dimethyldichlorosilane. Example 2 mentioned cotton cloth, exposed to similar vapors and treated with ammonia to neutralize free acid. It was claimed that the cotton cloth so treated was so water-repellant that it could be made into a bag to hold water and could be scrubbed with alcohol, acetone or aqueous soap solution without injury. It was suggested that materials of commerce could be covered or wrapped with cotton and the latter impregnated with the silicon compounds in this manner.

Paper, treated in this manner, retained its ability to absorb water but there was no disintegration.

In 1944, General Electric's U. S. Patent 2352974 (111) covered claims similar to those preceding with regard to electrical insulation, etc. In

addition it was suggested that these polymerized silicones might be useful when compounded with rubber, etc.

For a very exhaustive survey of the uses and methods of application of silicones, the reader is referred to Francis J. Norton's paper "Organo-Silicon Films" (273). "By a simple vapor treatment," literally thousands of pieces may readily be treated at a time, at low cost, to give a water-repellant surface. A mixture of crude methylchlorosilanes was used directly with a vapor pressure of about 200 mm at 25° C. This vapor reacts quite easily with water adsorbed on the surface of the material. Of course hydrochloric acid is given off and this may in some cases cause a limitation of the applicability of the process. A relative humidity of 50% to 90% was declared optimum. If water is actually visible on the surface, patches of hydrolyzed silicone will be unevenly distributed.

One coil was reported as having gained a silicone film 1.9×10^{-5} cm. in thickness. Another film was estimated as 5×10^{-5} cm. thick. One mole of dimethyldichlorosilane has been estimated to cover, after hydrolysis, 1.26×10^5 square meters of surface. Measurements on the molecular-scale model showed the thickness of a monomolecular layer of silicone on a given surface to be 6×10^{-8} cm.

A "convenient" method for this process is to bubble dry air through the methylchlorosilane and lead this mixture into some closed vessel containing the materials to be coated. There is, of course, an outlet to the vessel. Only a few minutes are needed but time must later be allowed for the escape of hydrochloric acid. Dr. Norton's Tables I and II are reproduced.

TESTS ON CERAMIC END PLATES

A. Pre-cooling + 100% Relative Humidity 25° C (Dewpoint conditions, with droplet condensation)

Resistance Megohms	Resistance Megohms
.1. Unglazed, untreated	3. Unglazed, methylchlorosilane treated
1.8	> 200,000
1.5	> 200,000
1.0	> 200,000
——	——
Av. 1.4	Av. = 200,000
2. Unglazed, waxed	4. Glazed, no other treatment
400	15
120	70
170	
——	
Av. 230	

B. No Pre-cooling + Approx. 100% Relative Humidity 25° C

1. Unglazed, untreated
   130
   650
   10,000

3. Unglazed, methylchlorosilane treated
   > 200,000
   > 200,000

2. Unglazed, waxed
   13,000
   5,500
   70,000

4. Glazed, no other treatment
   700
   2,400

GLAZED SURFACES—MEGOHMS RESISTANCE

	Chocolate Glaze	White Glaze A	White Glaze B
Condition of surface			
Dirty	0.5	0.75	0.4
Cleaned	48	2.8	2.6
$CCl_4 + C_2H_5OH$			
Treated by methylchlorosilanes	30,000—100,000—>200,000		

These methylchlorosilanes are, of course, flammable when mixed with air. The lower flammability limit for dimethyldichlorosilane and air was placed at $3.4\% \pm 0.1$ and for methyltrichlorosilane at $7.6\% \pm 0.3$. Ceramics with "metal inserts or connections" should not be considered. Ventilating conditions must be satisfactory. On the other hand, thousands of pieces may be treated at a time "at low unit cost" to give the water-repellant surface. There is very high surface electrical leakage resistance even under dew-point condensation conditions. In addition, the surface film is so thin that dimensions of the ceramic and of its holes are unaltered.

Water repellant properties of certain corresponding products from General Electric Co. were described in some detail in Chemical and Engineering News by Eugene G. Rochow (279). Paper, wood and cotton were discussed.

Arthur P. Laurie (615) has patented in the United States a method for the preservation of stone. The stone is soaked in an "undecomposed silicic ester dissolved in a volatile solvent" after which the moisture in the air is allowed to hydrolyze the silicon compound to provide an impervious coating, probably of hydrated silica. Tetraethoxysilane was mentioned as the ester.

Of more recent date, General Electric Co. (624) has covered by patent the production of slightly different water repellant materials as contrasted with tetraethoxysilane. However, these compounds and mixtures were also covered in Dr. Norton's paper, above (273). The material whose protection is desired is coated with a mixture consisting of about 2.8% to 99.2% of trimethylchlorosilane by weight and the remainder of tetrachlorosilane. "The exact nature of the invisible hydrophobic coating formed . . . .

is not known. A possible theoretical explanation is that the unhydrolyzed silicon chlorides react with moisture present on the surface of the body undergoing treatment to form a hydrophobic silicol or, silicone coating."

A General Electric paper (589) has reviewed the use of silicone resins in protective and decorative finishes, etc., where increased resistance is required to heat, chemicals and weather. Many of these have been modified with alkyd resins. Silicone paints may be compounded to give a high gloss and excellent color and tint. Of especial importance here is the absence of color in the resin and the freedom from discoloration during baking and curing. This general resistance to external influences constitutes the most outstanding property of silicone resins. Ultimate failure at any time is probably attributable to oxidation of the radicals, leaving silica.

Silicone alkyd resins however do not always show the resistance to these external conditions that the silicones themselves show. However, pigments which are usually considered unsuitable can be satisfactorily used in silicone resins. "Based on present knowledge the most heat-resistant silicone finishes are those pigmented with the conventional amount of aluminum powder." A table of data covering the heat resistance of silicone enamels was included.

General Electric's U. S. Patent 2386259 (379) dated October 9, 1945 covered the process of waterproofing materials by the use of hydrolysis products of methyldichlorosilane and methyldibromosilane. Later in the same year, there also appeared U. S. Patent 2388299 (380) describing further types of impregnations. Here the chlorosilanes were used on molds to render them waterproof and generally more satisfactory.

Yudin (611) has reported that clean iron strips, suspended in tetramethoxysilane, or its ethyl or propyl homologs, at 280°–300° for from 15 to 20 minutes, then taken out and heated at 80° (5 to 6 hours) in air and again in paraffine oil at 230°–240° (3 to 5 hours) are found to be coated with a colored, lustrous film. Films thus prepared from tetraethoxysilane were found most efficient as protective agents.

The Plaskon Co. (608) has patented a product formed from water, tetraethoxysilane and an "alkylated reaction product of urea and formaldehyde," in a solvent such as butyl alcohol. This product was found satisfactory for use as a lacquer amenable to heat hardening.

Another patent, du Pont's (610), described certain improvements in appearance and resistance of organic polymers by coating them with silicon polyethers, $Si(OR)_4$ where R may be methyl or any other radical up to $C_{12}H_{25}$.

Carbide and Carbon Chemicals Corp. (604) has patented the treatment of a surface, pre-treated with ammonium hydroxide, with a mixture of a

tetraalkoxysilane, water and a solvent for the polyether. One year later, in 1942, the Heaney Industrial Ceramic Co. (602) covered the preparation of vitreous, transparent, non-porous silica items by forming and firing an article of finely divided silica made by gaseous decomposition of silicon compounds.

C. P. Marsden, Jr. (597) patented the application of certain silicon condensation products to the inside of electric light bulbs. Before sealing, a mixture was applied consisting of a tetraalkoxysilane in a volatile solvent and then partially condensed by a strong acid such as hydrochloric. There must not be so much water present that the polyether is completely hydrolyzed. Silicone films of many other types have been applied to glass, as well (592). In this paper, work was reported covering studies of the contact angles of films on glass as well as the resistivity and "dry lubricity" of the surfaces. Considerable improvement was reported over the untreated glass. Thus contact angles of 90°–110° were readily obtained over a wide range of silicones used. It was found that the coefficient of friction for glass surfaces so treated (using alkyltrichlorosilanes) decreased with lengthening of the alkyl chain. Surface resistivity of the glass was improved from 10^{-8} or 10^{-9} to 10^{-12} or 10^{-13}. Methylsiloxanes showed greater thermal stability than those of other aliphatic groups, with phenyl about on a par.

Details were presented covering determination of the physical properties listed and discussed. Polysiloxanes of the type $(RSiHO)_x$ were used, prepared by hydrolysis of the corresponding dichloride $RSiHCl_2$. Alkoxyl groups were also present in some of these compounds while others were derivatives of $SiCl_4$ instead of $SiHCl_3$.

Montclair Research Corporation (663) has covered the waterproofing of a fabric by impregnation with a quaternary ammonium compound mixed with the product of the reaction between formaldehyde, tetrachlorosilane and some higher amide such as $C_{17}H_{35}CONH_2$.

The Continental Oil Co. (664) has described the addition to petroleum of various esters involving in the alcoholic section organic radicals containing silicon such as $C_6H_5Si(CH_3)_2CH_2$.

Remington Arms Co. (665) has coated steel ammunition with a corrosion resisting material made by hydrolyzing compounds of the general formula $(CH_3)_xSiCl_{4-x}$ where $x = 1$, 2 or 3. This type of treatment ensures against much of the corrosion of rain, hail, sleet, snow or salt spray.

Imperial Chemical Industries (666) has condensed straight or oil modified alkyd compounds with organic silicates. The products were heat resistant resins suitable for coating.

Corning Glass Works (667) has patented in Canada the preparation of a glass surface by coating with phenyltrichlorosilane preparatory to cover-

ing with a methyl methacrylate powder. Surfaces pre-treated in this manner were much more resistant to peel.

More than one type of tetraethoxysilane is available for commercial use (586)—"tetraethyl orthosilicate," "condensed tetraethyl orthosilicate" and "ethyl silicate 40."

Condensed ethyl silicate is satisfactory as an "investment binder for precision casting." It is manufactured from tetrachlorosilane in glass lined reaction chambers by the action of ethanol at a definite rate. Since the heat of reaction is greater than the heat of vaporization of hydrogen chloride, the temperature rises during synthesis. Variations in the manner of isolation result in the formation of different "polymerized" products.

"Ethyl Silicate 40" is capable of complete conversion of its ethoxyl groups to hydroxyls and further loss of water to form $(SiO_2)_x$. Details were given in this reference as to hydrolysis in hydrochloric acid. Hydrolysis in neutral solution was slow and in ammonia resulted in the formation of gels.

The material can be used for refractory binders, as impregnator for porous materials and for water proofing. Gels can be formed with liquids such as the lower alcohols, or acetone by the action of water and caustic. Pigmented solutions deposit films of great adhesive power.

"Sylon" (326), a product of the Minnesota Mining and Manufacturing Co., is available as RD602, a "clear, water white liquid" and RD611, a semi-solid. Water proofing ability is claimed for these products.

Corning Glass (601) has patented a combination coating of hydrolyzed tetraethoxysilane and synthetic resin, showing good adherence, wet or dry. In 1945 several additional practical applications of silicones to the ceramic industry (428) and to radio (431) were pointed out by Dow Corning Corporation.

Of late, as part of an entire series of contributions appearing in journals of limited circulation, descriptions have appeared of general applications. These include the field of the paper industry (483, 680), the electrical industry (457, 482, 677), paints and varnishes (464, 475, 476, 484, 682, 688), petroleum interests (486), plastics in general (473, 474, 487, 489, 495), engineering (466, 468, 470, 471, 478), aeronautics (469) metallurgy (472), water (477), general coatings (673) and ceramics (479, 686). Of more general interest are certain Russian contributions (465, 491) and a survey from England (461) as well as others (467, 490, 500, 501, 502, 503, 670, 674, 675, 676, 677, 678, 679, 681, 683, 684, 685, 687, 689, 692, 695).

Concerning Dow Corning Resins 993 and 2052, a company statement (275) has recommended the former for the purpose of impregnating transformer and other non-rotating coils, for the varnishing of fiberglas or "asbestos served magnet wire" and of fiberglas, mica and asbestos electrical insulating cloth, tapes, etc. The ability of resin 993 to resist heat and

moisture points it out especially for these purposes. Baking for one to three hours at 250° C was recommended after application. Resin 2052 will set with heat to a solid which will preserve its physical nature at 200° C. This resin was recommended for rotating equipment at high temperatures, again because of its resistance to moisture and heat. Baking for one to three hours at 200° C was suggested here as well.

As listed in a second bulletin (276) these fluids are water-white mobile, liquids, fluid even at "arctic temperatures." They possess an unusually low rate of vicosity change with temperature. They are stable to heat, neutral, chemically inert and non-corrosive to metals. The flash points of resins 993 and 2052 and similar compounds are higher than those of petroleum oils of equivalent viscosity. The resins easily wet clean, dry surfaces of glass, ceramics and metals, giving them water-repellant properties. Their resistance to oxidizing agents, mineral acids and corrosive salt solutions is high. There is no compatibility with rubber, rubber substitutes or organic plastics even at higher temperatures nor is there solvent effect. These materials are insoluble in water and the lower aliphatic alcohols but soluble in most other organic solvents. They are non-volatile, with the exception of those of lowest viscosity and there is a low dielectric constant and "power factor" over a wide frequency range.

Gardner and Westgate (281) of the National Paint, Varnish and Lacquer Association have investigated the catalytic curing of silicone resins, using Dow Corning's 993 and 2052. To a silicone resin in aromatic hydrocarbons was added a small amount of lead naphthenate. When the film was spread on a metal panel and dried under infra-red radiation the usual tackiness developed but was quickly hardened by ultra violet light. Without the lead naphthenate the residual tackiness did not disappear. Lead resinates and lead linoleate were also effective. The treated resin solution invariably gelled in a closed flask if left over night, hence it was believed that the action of the catalyst was one of condensation with or without polymerization, rather than oxidation. Further details will be found in the original paper. These products are available for use, according to statements, wherever there is a need "for a liquid which has a lower rate of change of viscosity with temperature than previously available oils, which will remain fluid at low temperatures, or which will be practically non volatile at elevated temperatures." Mention was also made of their value as insulating materials and their efficiency in the breaking of foams and the prevention of foam formation. Specific details along the same line were presented by the same authors (628) in another journal at about the same time.

"A silicone resin that normally required one hour's baking at 250° C. was cured in 15 minutes (air-dry) with an organic lead catalyst under infrared radiation. Studies were made on several silicone resins to determine the effects of: (1) organic vs.

inorganic lead compounds, (2) infrared vs. ultraviolet radiation and (3) combinations of infrared and ultraviolet radiation. Tack free films, both clear and pigmented, including an automobile finish, were obtained. They kept their flexibility, adhesion and color when subjected to temperatures above 300° C."

Previously, and as a foundation for the work reported above, extensive comparative problems had been undertaken along this line. Gardner and Bielous (625) found a combination of tetraethoxysilane and its analogous titanium compound, $Ti(OC_2H_5)_4$ were quite unsatisfactory after hydrolysis, on freshly made cement panels. In most cases, the coating dried and dusted off.

Gardner and Sward (626) in 1932 reported on the comparative value of hydrolyzed tetraethoxysilane as a protective coating for surfaces of buildings, art objects, etc. Van Heuckeroth (627) discussed the use of organic compounds of silicon in various lacquers. For example, a solution of cellulose nitrate in butyl acetate, diluted with toluene and plasticized with 50% dibutyl phthalate was treated with 85% of tetraethoxysilane, based on the cellulose nitrate content. After application to glass, it was found that the lacquer containing the silicon compound could not be stripped from the glass even after soaking in water 100 hours. Eventually, after stripping with a razor, slight etching of the glass was noticed. Tetraethoxysilane seemed to decrease the tensile strength of the lacquer but increased the elongation and adhesion.

General Electric Co. (623) patented, in 1946, the method of curing polysiloxane resins which involves lead monoxide. By this method what is probably a definite chemical compound was formed by the interaction of a silicone with hydroxyl groups and lead monoxide. Incidentally to the work, a crystalline compound $(CH_3)_3SiOPbOSi(CH_3)_3$ was isolated. The addition of lead monoxide "effected a reduction in both the curing time and temperature." Spongy products thus prepared were recommended for use as gaskets, etc.

Certain Dow Corning products have been amply described in a recent issue of "Plastics" (277). In HTS (high temperature silicone) operations 993 was most often mentioned. In general, this type of product can find application "(1) as an impregnant, coating and binder for fiberglas served magnet wire, (2) as a varnish for impregnating and coating fiberglas or asbestos cloth, tape and sleeving, (3) as an adhesive for bonding mica laminations to fiberglas or to asbestos cloth for ground insulation and (4) as a sealing varnish for filling voids and completely waterproofing assembled products."

Concerning liquids available, one may look for the following properties (1) the ability to wet clean dry glass surfaces, making them water repellant (2) high resistance to oxygen and oxidizing agents, mineral acids and cor-

rosive salt solutions, (3) incompatibility with rubber, rubber substitutes, etc., along with freedom from solvent effect even at elevated temperatures, (4) insolubility in water and other polar liquids including the lower aliphatic alcohols, but solubility in most other organic solvents, (5) low volatility, save for the low viscosity materials up to 400° F, (6) low dielectric constant and power factor over a wide frequency range, and (7) low change of viscosity with temperature, as compared with petroleum.

Data presented show a change in range of boiling points from 99.5° C to about 250° for a corresponding change in viscosity from 0.65 cstks to 100 at 25° C. The freezing points, covering the same change in viscosity ranged from −68° C to −55°, densities 0.7606 to 0.966 and refractive indices 1.3748 to 1.403. Coefficients of expansion varied, for the same range of viscosities from 1.598 to 0.994 and flash points from 30° F to 600° F. These data applied to the so-called Dow Corning silicone fluids of the 500 series.

Dow Corning products were further discussed in a recent issue of "Plastics" (277) and of Chemical and Engineering News (112). A special Dow Corning bulletin (278) covering ignition sealing compounds was put out by the company under date of October 25, 1944. "Dow Corning Silicones" (282, 690) dated 1945 and 1947, covered ignition sealing compounds once more and in addition, greases, fluids, varnish resins and rubber substitutes. A wealth of data was included in these bulletins, together with illustrations.

Corning Glass' U. S. Patent 2375998 (369) described the hydrolysis of methyltriethoxysilane to form, eventually, silicones adaptable to use as plastic materials. From the same source, U. S. Patents 2382082 (370) dated August 14, 1945 and 2398187 (375) issued in the following year covered polymeric silicones suitable for use as pressure fluids. Molding powders were covered in a British patent (265).

In U. S. Patent 2386467 (123) Corning Glass has described certain properties inherent in the polymeric methylphenyloxosilanes such as those which would make them valuable for the impregnation of glass fiber yarn. Experiments were described here showing the increase in flex resistance after impregnation. Again, in U. S. Patent 2390370 (442) there are claims as for instance "A strand composed of. . . . and an adhesive sufficient to bond the individual fibers together in strand form, the organic substituents of said organosiloxane being organic radicals attached to silicon through direct carbon linkage." U. S. Patent 2392805 (1946) (618) by Owens-Corning Fiberglas Corporation, described the preparation of a fiber glass coated, for optimum protection, with mixtures of various resins, silicones, etc., of several types. Objectives are fully realized using for instance "a coating comprising a combination of compounds selected

from the class consisting of hydrolyzable organo-silicanes or silanes, their hydrolysis products and their polymerized hydrolysis products or polysiloxanes. . . . " Specifically, silicon compounds found useful were polymerized ethylphenyloxosilane, dodecyltrichlorosilane, polymerized dimethyloxosilane, octadecyltrichlorosilane and "lauryl polysiloxane."

Arthur D. Little, Inc. (598) has patented the preparation of compounds of the type $Si(OR)_4$ where R is phenyl, tolyl or other aryl radical and their mixtures with other silicon compounds for use as heat transfer media.

The writer of this review is indebted to Mr. Matthew Hayes of the Houde Engineering Division, Houdaille-Hershey Corp., Buffalo, N. Y., for a summary of two interesting articles which appeared in the Transactions of the American Society of Mechanical Engineers of recent date.

"In the search for low- and high-temperature lubricants and noninflammable hydraulic fluids, the Naval Research Laboratory (336) studied dimethyl silicone polymer fluids. It was found that all of the nonferrous bearings including copper-lead, bronze, commercial brass, babbitt, copper, aluminum 17S and Alfin alloy performed satisfactorily with silicone fluid especially with chromium plated high-carbon steel journals. Cast iron or steel bearings used with steel journals were quick failures. During the break-in process an organic silicone film was formed which increased the load carrying capacity of the same bearings when operated with petroleum lubricating oils. This film may be built up more rapidly by pretreating or lacquering the bearings with a silicone before assembly of the test machine."

The second paper (337) was of the same type.

"These silicone fluids give excellent results when used as hydraulic media in gear or piston pumps if either or both loaded surfaces are nonferrous. Very little wear was shown, however, on steel to steel rolling friction such as bearing races. A simple slider and plate test was developed which quickly separated good and bad bearing combinations used with silicone fluids. A protective film was formed on bronze bushings similar to that found on the journal bearings discussed in the preceding paper. A satisfactory pipe-thread sealant was found which would prevent the leaking and creeping of silicone fluids.

General Electric Co. has found that faster and better production of molded mica parts is possible with the use of silicone oils as "mold release agents" (341).

Cogan and Stetterstrom (340) of the Mellon Institute have presented a survey, with bibliography, of some of the physical and physiological properties of tetraethoxysilane. For the most part the physical properties listed cover the hydrolysis products of this polyether. Certain applications of the ether are also discussed.

Chemical and Engineering News (353) listed a new silicone paint, about

to be put on the market by General Electric Co., suitable for automobiles, refrigerators, electric ranges, etc.

Monsanto Chemical Co. (480) uses organo silicon resins as binding compounds for abrasives thereby obtaining higher grinding speeds. Koff and Frederick (481) found Dow Corning stopcock grease satisfactory for apparatus used in work on thiamine.

A French patent (538) covered the use of compounds hydrolyzing to silica, as agents for the sealing of gas or oil wells. Organic compounds of silicon are also of value as lubricants (557, 540). North American Rayon Co. (541) co-polymerized certain organic compounds of silicon with viscose or cuprammonium cellulose.

Shappiro (533) has patented the use of certain compounds such as SiR_4 as antiknocking agents. R should be olefinic and not more than four carbons in length.

Frank J. Sowa (638) assigning to International Engineering Corporation, has patented an "Antiknock Fuel" containing organic silicon. Compounds were preferred which had only one group attached to silicon which was susceptible to hydrolysis to hydroxyl. Otherwise linear polymers could be formed which might interfere with the desirable anti-knocking properties. Thus compounds of the general formula R_3SiOR were quite acceptable. One of the most interesting sections of this patent appeared near the end. The author stated that the increase in octane value was not noticeable immediately but soon made its appearance, and persisted after the use of the organic silicon compound had been discontinued. He interpreted these observations to mean that accelerating surfaces were formed in the cylinder. It was also stated that these organic silicon compounds "clean out carbon deposits in the engine cylinders by causing it to flake or by accelerating its oxidation."

Corning Glass (600) has covered a process by which a hydrolyzable silicon compound such as tetramethoxysilane or tetraethoxysilane is vaporized into a high temperature flame of some combustible gas and oxygen. The flame is brought to bear on a refractory surface depositing silica in the desired shape and size which is then vitrified to transparency at 1000°–1400°.

In U. S. Patent 2388161 (125), American Cyanamide's, describing the preparation of tetraallylsilane, it was stated that "polymers of tetraallylsilane or copolymers thereof are useful in coating compositions, castings, moldings, as adhesives and in laminating. Various organic and inorganic fillers may be included in molding compositions such as alpha cellulose pulp, wood fiber, asbestos, glass and mica." Adhesion to glass was also described separately.

Silicone fluids (285) are now being used to dampen the vibration of

crankshafts on automobile and Diesel engines by the Houdaille-Hershey Co., developed at the Houde Engineering Division, Buffalo, N. Y., by Bernard O'Connor. Applications of silicone resinous materials to high temperature insulation (286) is becoming a feature with Westinghouse Electric Corporation.

Whether made up with or without solvents, certain general statements can be made of the varnish materials as described. Inasmuch as these silicone varnishes require, under normal conditions, temperatures of 225°–275° for curing, it is essential that a minimum of organic material be present in the insulation. This precludes the use of organic resins with silicone varnishes for insulation purposes. "The superiority of silicone varnished glass cloth as compared with a Standard Class B varnished glass cloth after twenty four hours at 250° C has been demonstrated." The silicone will be found to have retained "its original flexibility," while the "Class B" material will be slightly darkened and somewhat brittle.

At the same time, some of these low-viscosity silicone fluids are excellent water repellants, preventing the formation of a continuous film on the treated surface.

The article listed three ways in which "thermal endurance properties may be utilized."

"(1) . . . a reduction in size and weight of electrical equipment is possible where the operating temperature can be increased and where no reduction in insulation life can be tolerated; (2) increased service-life of the insulation can be obtained where it is desirable to maintain conventional size, weight and temperature limits; and (3) operation in ambient temperatures above the permissable limits for conventional types of insulation can be maintained."

Specific examples were listed.

B. F. Goodrich (287) has presented "Silica White" as a new ingredient in rubber compounding, a sort of "white carbon black." It is claimed to produce the same qualities as carbon black itself but without the color. The particles have the same size and shape as do those of carbon black of superfine type and impart increased tear resistance, abrasion resistance and tensil strength without affecting color.

Concerning the stability of polymethylsiloxanes (593) to oxidation, it has been reported that no change occurs below 175°. At 200° oxidation is shown by changes in viscosity with evolution of HCHO and HCOOH. Increase in viscosity was attributed to condensation of two or more siloxane radicals from which methyls had been burned off. Copper, lead and selenium inhibit oxidation at 200°. Copper and selenium also inhibit changes in viscosity while tellurium accelerates oxidation. High evaporation losses when lead is used were explained on the assumption of the following reaction:

$$(CH_3)_3Si(OSi(CH_3)_2)_nOSi(CH_3)_3 + PbO = \begin{matrix} (CH_3)_3Si(OSi(CH_3)_2)_xO \\ (CH_3)_3Si(OSi(CH_3)_2)_yO \end{matrix} \Big\rangle Pb.$$
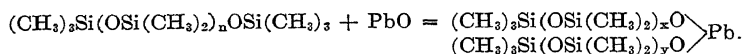
Charts were presented showing variation of yields of formaldehyde and formic acid from various polysilicones on dynamic oxidation plotted against time at 200°, as well as the same for static oxidation.

The Naval Research Laboratories (594) of Washington, D. C., have reported continued studies on the surface active properties of "polyorganosiloxanes." This study covered densities and surface tensions, along with their coefficients, also the spreading pressures of silicones. In addition, some attention was paid to the force-area and potential-area relations of monomers, on water, of various types of linear compounds of this type.

A qualitative explanation was presented here for the variation in viscosity with substituents, including the unusually high values of methyl compounds. It was suggested here also that the larger diameter "of the silicon atom as compared with the carbon atom is responsible for the

Table 15

1,1-Dichloroethane	20
Tetrachloroethylene	12
Carbon tetrachloride	8
Trichloroethylene	7
1,1,2-Trichloroethane	2
Acetone	2
Decahydronaphthalene	2
1,2-Dichloroethane	1
Ethyl alcohol	0.1
Methyl alcohol	0.1

greater ability of the polymethylsiloxanes to coil, as compared with analogous linear polymers of the hydrocarbon or ether type." The larger size of silicon, as compared with carbon, permits a certain freedom of rotation which would not be expected in analogous types. It was also stated that at low film pressures each helix uncoils and the molecule adsorbs with the long axis in the water. The length of this helix increases with temperature. Data on electric moment per monomer unit were presented and discussed.

Types studied in the course of this work included polymethylsiloxanes, linear polyethylsiloxanes and linear polymethylphenylsiloxanes.

A simple laboratory procedure for the removal of silicone stopcock grease from glass surfaces has recently been described by Constabaris (325). Complete details are to be found in the original paper.

The Ethyl Corporation, at Baton Rouge, La., (523) has reported a "highly satisfactory" procedure for the removal of Dow-Corning stopcock grease from glass ware. 1,1-Dichloroethane dissolves about 20% at 29° C. Other solubilities were also listed, as weight % of silicone grease at 29° C.

Cities Service Oil Co., (488) has patented a fluid, satisfactory for use in compasses, etc., over a wide temperature range.   It consists of a mixture of 50 volumes of 1-nitropropane, 20 volumes of tetraethoxysilane and 30 volumes of 1,2,4-trimethylbenzene.   F. J. Sowa (463, 498) has covered the addition of organic silicon compounds to mineral oils (1% to 50%) to improve the viscosity, oiliness and other properties.   Amyltriethoxysilane may be used.

Shell Development Co. (459, 494) has patented the suppression or elimination of foaming in oil-in-water emulsions by the addition of 0.0005% to 0.5% of silicone polymer.

E. I. du Pont de Nemours and Co. (639, 640) has covered the use of silica, especially prepared, in tanning.   According to Rose (643), although "no process in which silicon compounds were the principal agent has reached the commercial stage," tetramethoxysilane and tetraethoxysilane were found to have a marked tanning action upon hydrolysis in dehydrated or pretanned pelt.

Carbide and Carbon Chemicals Corp. (605) has patented the formation of an inflammable gel, or canned heat by the mixing of ethyl alcohol, sodium hydroxide and a silicon polyether such as tetraethoxysilane.   Two other patents (606, 607) covered the preparation of an adhesive material from silica, in turn made by the hydrolysis of a tetraalkoxysilane, for instance of glycol or glycerol.   Pittsburgh Plate Glass (599) has described the mixing of vinyl acetal or vinyl butyral resin with partially hydrolyzed tetraethoxysilane, and water.   This composition was found satisfactory for waterproofing and for laminating wood, glass, metals, etc.   Adhesion of silicones to glass has also been discussed in recent symposia (586).

The Radio Corporation of America has patented (609) a luminescent material, made by dispersing a selected metallic oxide in a salt of some fourth column element.   For example zinc oxide is suspended in a partially hydrolyzed solution of tetraethoxysilane.   Eventually silica precipitates on the zinc oxide with heating.   Fluorescent silicon compounds have been prepared by General Electric Corporation (603) by hydrolyzing, for instance, tetraethoxysilane and zinc nitrate with a fluorescence activator such as manganous nitrate.   The process was completed by heat.

Austenal Laboratories (616) have covered the preparation of a dental mold material of which an "organic silicate" was one of the original constituents.   Some of the claims were later modified.

General Electric's Plastics Division (280) has presented a pamphlet covering its "Silicone Rubber," ". . . . the youngest member of the silicone family developed."   Apparently dimethyldihydroxysilane was the monomer.   There is a retention of the properties which classify it as a rubber substitute even after four months of heating at 400° F and after forty eight

hours at 575° F. Resistance to standard and improvised conditions of aging is very satisfactory. When immersed in a carbon dioxide-acetone bath whose temperature was gradually lowered to −82° F there was no appreciable change in flexibility. At −90° F the flexibility decreased but the material was not brittle. Silicone rubbers are made in almost any degree of hardness from 25 to 80, as tested by the Shore "A" Durometer. The most desirable recommended values lie between 45 and 60. Compression Set, as measured by a modification of the "A.S.T.M. method D395-40T," was described by a series of curves. Approximately 50% compression set was attained at 302° F at the end of 1.75 days and the curve levelled off just below 90% beyond 22 days. At low temperatures, there was marked rise (above 10%) below −200° F.

"The tensile strength of silicone rubber is lower than that of most other rubbers." In contact with strong acids and alkalies, silicone rubber goes to pieces rather rapidly. There is swelling in hydrocarbon solvents, greater in the aromatic. There is less swelling with polar solvents such as alcohols, phenols, chlorinated hydrocarbons and nitro compounds.

Working with silicone rubber containing silica as a filler, considerable data have been accumulated.

"The decrease in dielectric constant on increasing the temperature from 25° C to 100° C is caused by a change in density. The dielectric constant of this rubber is only slightly higher after conditioning in 100 percent relative humidity at 25° C for three days."

Over the frequency range measured, the loss factor at 100° C was found to be only slightly greater than the values obtained at 25° C and as a general consideration, the loss factor of the "wet" sample was found to be only slightly higher than that of the "dry."

Resistance to ozone and corona conditions is high. Under comparable conditions, surface cracks do not appear as do in Buna S.

" The property of low compression set at elevated temperatures coupled with the heat resistance of the rubber makes it a desirable gasket material for high temperature operation. Most of the applications to date take full advantage of these properties, including gaskets for turbo-superchargers, Naval searchlights and signal lights, chemical manufacturing equipment and electrical apparatus. The superior ozone resistance and chemical resistance properties are taken advantage of in some applications where the high temperature properties are not a necessity. Results indicate that the temperature flexibility and lack of corrosive action is a prime requisite."

Further details (365) may be found elsewhere.

Dow Corning's Silastic is described in Bulletin 1-A of 1946 (420). Again, the general characteristics of organic compounds of silicon come to the fore in that silastic retains its rubber-like properties at temperatures much higher than those which would cause other, natural rubbers and rubber

substitutes to decompose, 500° F "and upward." Silastic is flexible as low as −70° F. It can be molded, extruded or applied as a coating for glass cloth, metal or wire. Consequently it is of use as an electrical insulating material and a bonding agent. Some of the data in this pamphlet showed practically no variation of elasticity with time, when the samples were heated at 250° C. Tensil strength only began to fall at the end of the first twenty four hours. Its fireproof qualities were also listed. Considerable information was also given on the action of various laboratory reagents on silastic.

A more compact chart was presented by Bass, Hunter and Kauppi (429).

CHEMICAL RESISTANCE OF SILASTIC

| | Coating and Laminating | | | | Type | Molding and Extruding | | | | |
	120	121	125	125 Red	150	160	160 Red	167	180	181
HOH	G	G	G	G	G	G	G	G	G	G
HOOH, 3%	G	G	G	G	G	G	G	G	G	G
NH₄OH, 10%	G	G	G	G	G	G	G	G	G	G
NH₄OH, conc.	F	G	F	G	G	G	G	G	G	G
NaOH, 10%	P	F	P	F	F	P	P	P	G	G
NaOH, 50%	G	G	G	G	G	G	G	G	G	G
Na₂CO₃, 2%	G	G	G	G	G	G	G	G	G	G
NaCl, 10%	G	G	G	G	G	G	G	G	G	G
H₂SO₄, 10%	P	G	P	G	P	P	F	P	G	G
H₂SO₄, 30%	—	G	—	G	—	—	—	—	G	G
H₂SO₄, conc.	P	P	P	P	P	P	P	P	G	P
HNO₃, 10%	F	G	F	G	G	G	G	P	G	G
HNO₃, conc.	P	P	P	P	P	P	P	P	F	G
HCl, 10%	F	G	F	G	G	F	G	P	G	G
HCl, concl.	P	P	P	P	P	P	P	P	F	G
CH₃COOH, 5%	G	G	G	G	P	F	F	G	G	G
CH₃COOH, conc.	G	G	G	G	P	P	F	G	G	G
C₆H₅CH₃	P	P	P	P	P	P	P	P	P	P
CH₃COCH₃	G	G	G	G	G	F	G	F	G	G
Gasoline	P	P	P	P	P	P	P	P	P	P
Stoddard Solvent	P	P	P	P	P	P	P	P	P	P
Mineral Oil	G	G	G	G	G	G	G	G	G	G
CCl₄	P	P	P	P	P	P	P	P	P	P

F = fair, G = good, P = poor.

A private communication (706) has summarized the properties of Dow Corning silastics still further.

"The K values given may be used to convert the dial readings to lbs./in. It is to be noted that the 'return' values do not follow the theoretical form in that they

apparently return to the origin instead of crossing the x-axis to the right of the origin, this discrepancy being due to the limitations of the measuring equipment used. However, to give an idea of where the return curve should cross the x-axis, the residual elongation, after removal from the tensile tester (Scott, Model L-6) has been noted.

Hysteresis Loss

Silastic 150

Elongation	50%	100%	150%	200%	250%	300%	350%
Scale Rdg.	1.5	4	6	7.3	8.66	9.4	10.2
	2	2.5	3.5	4	5	6	Return

K = 21.7

Residual Elongation = 20%

Silastic 160

Elongation	20%	40%	60%	80%	100%	120%	140%	160%
Scale Rdg.	1.3	4.4	6.6	8.8	11.2	14.5	17.2	19.9
	1.6	2.8	3.5	4.4	5.4	6.8	8.2	

K = 23.9

Residual Elongation = 8%

Silastic 180

Elongation	10%	20%	30%	40%
Scale Rdg.	4.6	14.6	21.8	27.8
	5	7	10	

K = 20.87

Residual Elongation = 3%

All three silicone rubbers above were cured for an equal period. More highly cured samples have decreased residual elongation in all cases. The residual elongation is not permanent, nearly disappearing after 48 hours."

Further applications of silicon compounds to the field of elastomers will be found in more technical literature (462, 492, 493). B. F. Goodrich Co. (596) has patented the use of polymethyl and ethyl silicon compounds, as combustible materials, burning to silica of particle size less than 0.1 mu. These particles were described as of value as reinforcing agents in vulcanized rubber. In addition, tetraethoxysilane was burned in jet-type burners, mixed with equal volumes of illuminating gas.

The Connecticut Hard Rubber Co. (588) has reported investigations into the character of certain types of silicone rubber. Bond energies are reported as

C—C	58.6	C—O	20.0
Si—C	57.6	Si—O	89.3,

and with these in mind it is not difficult to visualize the stability of silicon elastomers, even though they are composed of such large aggregates of monomers. Tensile strength of silicon elastomers is increased by titanium dioxide filler but even so, the data given herein would indicate that this increase is no greater than that of other types of stock. Extensive discus-

sions of physical properties were included in this paper as well as variations of these properties with temperature.

"Silicone rubbers will adhere to a properly prepared glass surface with a force which is greater than the breaking strength of the rubber itself (over 600 lbs/sq in)."

Swelling in solvents is a function of the solvent and is influenced as well by the amount of filler in the rubber.   Of six solvents, carbon tetrachloride caused the greatest percent swelling while water caused the least.   Electrical properties were retained over a temperature range of from −65° to 200° C.   The paper closed with a discussion of the uses of silastic as hydraulic seals, belting, coating of fabrics, gaskets and in electrical devices.

Konkle, Selfridge and Servais (595) have studied the heat resistance of silicone rubbers, a property considerably more outstanding, as indicated above, than the same in ordinary rubber stocks.   It was suggested that heat resistance is greater because "resistance to one set of conditions is not developed by special formulation at the expense of resistance to other kinds of aging."   Weather and oil resistance were also studied, as well as low temperature flexibility.   In figure 2, of this paper, it was shown that GR-M, heated at 300° for not more than one hour lost 8% of its weight while silastic (3 samples) after more than eighty hours at this temperature lost between 3.6% and 4.3%.   Plotted data covering oil resistance, weathering resistance, low temperatures and oven aging were most interesting and only lack of space forbids their more extensive exposition at this point.

One section of a recent Dow Corning pamphlet (278) was given over entirely to a presentation of certain physiological properties of commercial silicones used as ignition sealing compounds.

"Dow Corning No. 4 compound is practically inert from a physiological standpoint.

The physiological response of laboratory animals to the oral administration of single doses of Dow Corning No. 4 Compound indicates that there is no hazard from the oral ingestion of single doses of this material.   Physiological response to repeated ingestions has not been determined.

Tests were made on laboratory animals to determine whether Dow Corning No. 4 Compound had skin irritating properties.   In no case was there evidence to indicate that any of this material by itself would cause an appreciable skin irritation.   This is confirmed by the experience of a variety of workers in daily contact with the material over a period of several months.

Dow Corning No. 4 Compound is not an immediate irritant of the eyes.   That is, there is no apparent irritation at the time of contact but the conjunctival membranes become inflamed several hours afterward.

This irritation may persist for a few hours, after which it subsides.   The sensation, like that resulting from continually facing a strong wind, usually disappears after a night of sleep.   Since the Dow Corning No. 4 Compound has a negligible vapor pressure at room temperature, the most likely source of contact with the eyes is by rubbing them with contaminated hands.   It is recommended therefore that ordinary cleanliness be observed in the handling of the material."

General Electric Co. (662) in U. S. Patent 2426912 (1947) has described the hydrolysis of dimethyldihalogenosilanes by pouring on the surface of a swirling solution of an electrolyte by which the silicon compound is hydrolyzed and polymerized. These polymers are of fairly high molecular weight, less than 10% boiling below 200°, and the majority are suitable as elastomers.

Bergendahl and Libby (680) have reported the results of investigations into the use of silicones in the beater sizing of paper. The abstract is quoted below.

"The synthetic resins have been of interest to the papermaker for some time as a possible substitute for rosin in sizing paper. Among the synthetic resins now available, one group in particular, the silicones, has attracted attention through their many unusual properties, i.e., stability against heat, resistance against chemicals and water.

The first use of the silicones in the paper industry took place during World War II when gas mask filter paper was treated with the vapor from methylchlorosilane. Sizing obtained by this method is excellent but certain disadvantages are connected with the use of the vapor sizing method. Therefore, in this investigation a number of other silicones have been tested regarding their suitability as beater sizing agents.

It was found that one of the silicones, a fast curing resin in a toluene solution, gave very satisfactory sizing both to water and ink. The amount of resin necessary using distilled water in the beating and sheet making procedures was less than 0.1%. It was found also that a mixture of the fast curing resin and an alkaline or acidic emulsion of methylsilicone oil gave good sizing results. Sizing was obtained when the silicone was added to the pulp stock at a pH value below 7.0. The final pH was not of any importance.

The silicones may be used in sizing the most common types of papermaking pulp and the freeness of the pulp does not affect the sizing result.

The type of water used during the refining and papermaking process is of great importance. A hard water will decrease the sizing effect of the silicones.

The small amount of silicone necessary for good sizing makes the silicones especially suited for the sizing of paper where a large amount of size might cause difficulties."

General Electric's Dri-Films 9978, 9980, 9990, 81039, 81040 and 81041 were used as well as Dow Corning's 2103.

Chapter 8

Silico Organic Compounds Analogous to
Ethers and Amines

The chemistry of compounds containing silicon connected to at least one alkoxyl or aroxyl group and of the corresponding compounds with sulfur or selenium in place of oxygen has been covered in the ACS Monograph "Chemistry of Aliphatic Orthoesters" (84), and for that reason this chapter will concern itself for the most part only with references not touched upon therein.

In 1858, Knop (293) reported the action of ethanol "with not more than 5 per cent water" on tetrafluorosilane. Probably the product was tetraethoxysilane, but Knop's figures were so different from what this product would have required using modern atomic weights, etc., that an accurate appraisal of his results is difficult.

In connection with work on the atomic weight of silicon, Friedel and Crafts (118) also reported the action of ethanol on tetrachlorosilane. Disproportionation was discovered between tetrachloro- and tetraethoxysilane and reactions reported with acetyl chloride and acetic anhydride:

$$4C_2H_5OH + SiCl_4 \rightarrow Si(OC_2H_5)_4 + 4HCl$$
$$3C_2H_5OH + SiCl_4 \rightarrow ClSi(OC_2H_5)_3 + 3HCl$$

$$Si(OC_2H_5)_4 + SiCl_4 \rightarrow 2Cl_2Si(OC_2H_5)_2$$
$$2ClSi(OC_2H_5)_3 + SiCl_4 \rightarrow 3Cl_2Si(OC_2H_5)_2$$

$$Si(OC_2H_5)_4 + CH_3COCl \rightarrow ClSi(OC_2H_5)_3 + CH_3COOC_2H_5$$
$$Si(OC_2H_5)_4 + (CH_3CO)_2O \rightarrow CH_3COOSi(OC_2H_5)_3 + CH_3COOC_2H_5$$
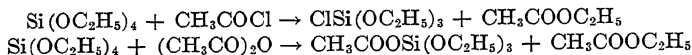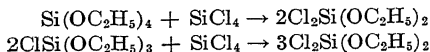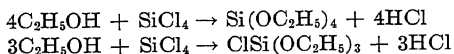
Later, Friedel and Ladenburg (64) prepared hexaethoxydisiloxane

$$Cl_3SiOSiCl_3 + 6C_2H_5OH \rightarrow 6HCl + (C_2H_5)_3SiOSi(OC_2H_5)_3$$
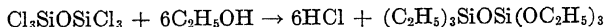
The reaction was strongly endothermic.

Ladenburg (408) also prepared phenyltriethoxysilane by the action of anhydrous ethanol on phenyltrichlorosilane. The product was easily hydrolyzed to the silicon compound which could be considered the counterpart of benzoic acid, isolated after caustic addition and precipitation by carbon dioxide as the corresponding anhydride $(C_6H_5SiO)_2O$. This compound, 1,3-diphenyl-1,3-dioxodisiloxane, gave rise to flammable gases

122

when heated in air. The disiloxane was soluble in ether and alcohol but only slightly soluble in water. It was also soluble in sodium hydroxide solution but could not be reprecipitated on addition of hydrochloric acid.

Troost and Hautefeuille (359) treated hexachlorodisiloxane and (probably) octachlorocyclotetrasiloxane with absolute alcohol. The products were, as expected, $(C_2H_5O)_3SiOSi(OC_2H_5)_3$ and $(C_2H_5O)_8Si_4O_4$.

In 1898, Abati (443) prepared tetramethoxysilane by the method of Friedel and Crafts (60) and of von Ebelman (444), and also tetraethoxysilane and tetrapropoxysilane by the same method. Hexapropoxydisiloxane was found as a by-product of the last synthesis. These compounds, with others, were used in Abati's studies on the atomic refraction of silicon.

In 1901, Kipping (1) found that menthol, phenol, eugenol and methanol would react with a chlorosilane replacing the halogen with the appropriate alkoxyl or aroxyl group. He also described the reaction between triphenylhydroxysilane and acetyl chloride by which acetoxytriphenylsilane was formed.

Walther Dilthey (294) in 1903 called attention to the work of von Baeyer and Villiger (298) on relative basicities of alcohols and described the action of tetrachlorosilane on triphenylcarbinol by which not tetra-triphenylmethoxysilane but orthosilicic acid was formed:

$$4(C_6H_5)_3COH + SiCl_4 \rightarrow 4(C_6H_5)_3SiCl + Si(OH)_4$$
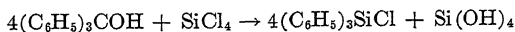
Acetylacetone reacted in chloroform solution with violent evolution of hydrogen chloride:

$$3(CH_3CO)_2CH_2 + SiCl_4 \rightarrow 3HCl + (C_5H_7O_2)_3SiCl$$
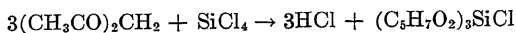
The pure product was not isolable because of its marked tendency to add hydrogen chloride in the molar ratio of 1:1. Dilthey was unable to move the fourth chlorine in tetrachlorosilane. The extra molecule of hydrogen chloride could be moved, however, by ferric chloride, gold chloride or platinum chloride to give nicely crystalline double salts of the formula $(RO)_3SiFeCl_4$, $(RO)_3SiAuCl_4$ or $[(RO)_3Si]_2PtCl_6$. Complete experimental details were given in the original paper.

Dilthey's second paper of this group (295) reported two forms of the ferric chloride double salt, using benzoylacetone. These forms were not interconvertible and were therefore not dimorphic, but rather to be regarded as isomeric. The isomers were also found when gold chloride and zinc chloride were used instead of iron, but not when the two groups of the diketone were identical, as with diacetylmethane or dibenzoylmethane. Dilthey at first offered the suggestion that these isomers were enol ethers

and that in one case the oxygen nearer the phenyl had shifted to enol and in the other the one nearer the methyl:

$$CH_3—C{=}O$$
$$\diagdown CH \quad and \quad$$
$$C_6H_5—C{\!/\!/}—O—H$$

$$CH_3—C—O—H$$
$$\diagdown\!\!\diagdown CH$$
$$C_6H_5—C{=}O$$
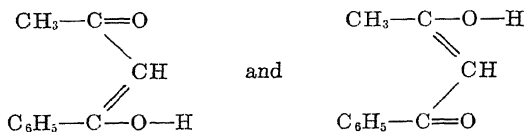
If these compounds contained linkages through replacement of hydrogen attached to carbon (keto form) molecular asymmetry would have resulted. No mention was made of any attempted resolution into optically active forms.

The third paper in the same year (296) described the action of hydrobromic acid in acetic acid or chloroform on compounds such as those listed above, of the general formula $(RO)_3SiCl$, by which hydrogen chloride was given off and the silicon compound converted to the bromide. Hydrogen iodide had the same effect. The iodide $(RO)_3SiI$ possessed the interesting property of adding iodine to form a periodide. The picrate could also be prepared in the same manner and treatment of $(RO)_3SiCl$ with silver nitrate precipitated silver chloride with formation of a complex salt $[(RO)_3SiONO_2]_2(AgONO_2)$. The acid sulfate was made from the chloride by the action of sulfuric acid. Tetrabromosilane behaved as did the tetrachloro- compound.

In the fourth and final paper of this group (297) appearing in 1905, Dilthey presented in effect a comparative review of what he termed "onium" compounds of silicon, boron and titanium. By "onium" compounds was meant compounds with co-ordinate valences beyond the usual value, or Werner complexes. Dilthey here wrote the formulas of the silicon compounds in a three-dimensional manner to show possible isomerism with the anion completely ionized, much in the same manner in which similar complexes have been written for cobalt, etc. In more modern terminology, the attachments between carbonyl oxygen and silicon would be termed dative bonds and the structures chelated. This formula makes quite logical the addition of ferric chloride to chloride ion to form the anion $(FeCl_4)^-$, but does not make particularly plausible the addition of HCl.

Analogous results were obtained some time later by Rheinboldt and Wisfeld (139) working with hexachlorodisiloxane. Acetylacetone formed the same type of product $[(RO)_3Si]$ $(FeCl_4)$.

Rosenheim and co-workers (545) reported preparation of $[(C_5H_7O_2)_3SiCl]$ (HCl) after refluxing. The analogous compound from ethyl acetoacetate melted at 96° to 98°.

Grüttner and Cauer (192) in 1918 prepared *p*-bromophenyltrimethoxysilane by the action of methanol on *p*-bromophenyltrichlorosilane. The

corresponding triethoxy, tripropoxy and tri-i-butoxy compounds as well as phenyl-p-bromophenyldiethoxysilane were also synthesized by the same method. As a by-product in the last synthesis there was isolated 1,3-diphenyl-1,3-di-p-bromophenyl-1,3-diethoxydisiloxane.

In 1927, Jörg and Stetter (83) allowed phenol to react with tetrachlorosilane at 100° to form diphenoxydichlorosilane, triphenoxychlorosilane and tetraphenoxysilane. In similar manner there were also prepared tetra-p-bromophenoxysilane and tri-p-bromophenoxychlorosilane. Triphenoxychlorosilane reacted with phenylmagnesium bromide giving triphenoxyphenylsilane, as did phenyltrichlorosilane and phenol. p-Methoxyphenol reacted with tetrachlorosilane forming tetra-p-methoxyphenoxysilane. Phenyl mercaptan gave a very small yield of phenylmercaptotrichlorosilane.

Diphenyldichlorosilane reacted with phenol in benzene (37). After heating the mixture for three hours at 200°, Kipping isolated diphenylphenoxychlorosilane. This compound fumed in moist air, giving hexaphenylcyclotrisiloxane. Diphenoxyphenylchlorosilane was also formed by the action of phenol on diphenyldichlorosilane in benzene along with the products mentioned above. Continuing this study, Kipping and Murray (38) found that even at room temperatures diethyl ether reacted slightly with tetrachlorosilane, forming ethoxytrichlorosilane and ethyl chloride. Ethoxytrichlorosilane could not be separated from tetrachlorosilane. Similarly, diphenyldichlorosilane formed diphenyldiethoxysilane. Ethanol did not react with diphenyldichlorosilane without heating.

Kipping (42) investigated the action of phenol on tetrachlorosilane with positive results. All four possible products were obtained: phenoxytrichlorosilane 20 per cent yield, easily hydrolyzable in water; diphenoxydichlorosilane 35 to 40 per cent yields, also fuming in air; triphenoxychlorosilane 35 per cent yield fuming slightly in air; and tetraphenoxysilane in 2 to 5 per cent yields. The three compounds listed above which contain chlorine all reacted with sodium, but tetraphenoxysilane was the only isolable product. In this manner, however, all the phenoxide was accounted for. It was assumed that sodium first reacted to form sodium phenoxide, which then in turn reacted with chlorine attached to silicon in the conventional manner.

Sugden and Wilkins (409) prepared tetramethoxysilane and tetraethoxysilane by the action of the proper alcohol on tetrachlorosilane. The polyethers were used in determinations of the atomic parachor of silicon.

Uchida and Kondo (299) allowed menthol to react with tetrachlorosilane forming menthoxytrichlorosilane, dimenthoxydichlorosilane, trimenthoxychlorosilane and tetramenthoxysilane. The atomic refraction of silicon was calculated as 5.114.

Schumb and Holloway (143) prepared a series of chlorooxosilanes and their respective ethoxyl derivatives.   By the action of a mixture of chlorine and oxygen on silicon heated to redness the following were prepared: Si_2OCl_6, $Si_3O_2Cl_8$, $Si_4O_4Cl_8$, $Si_4O_3Cl_{10}$, $Si_5O_4Cl_{12}$, $Si_6O_5Cl_{14}$ and $Si_7O_6Cl_{16}$. All except $(SiOCl_2)_4$, which was a crystalline solid, were oily liquids soluble in carbon tetrachloride, chloroform, carbon disulfide or tetrachlorosilane. All hydrolyzed with moisture.   Absolute alcohol reacting with the appropriate halide formed $Si_2O(OC_2H_5)_6$, $Si_3O_2(OC_2H_5)_8$, $Si_4O_3(OC_2H_5)_{10}$, $Si_6O_5(OC_2H_5)_{14}$.   These compounds could not be directly prepared from the oxobromides, but the method was successful using sodium ethoxide. The use of alcohol instead of sodium ethoxide caused formation of hydrobromic acid as a by-product.   This acid reacted with ethanol taking the latter out of circulation and forming ethyl chloride and water, with consequent hydrolysis of silicon compounds.   Schumb and Stevens (655), con-

Table 16.

Molar ratio SiCl₄/alcohol	% Yields.			
	RoSiCl₃	(RO)₂SiCl₂	(RO)₃SiCl	(RO)₄Si
2.35	66.5	4.9	1.9	0.0
0.35	0.0	32		0.0
0.25	0.0	0.0	0.0	60.0

tinuing reference 143 studied the partial alcoholysis of tetrachlorosilane preparing ethoxytrichlorosilane, diethoxydichlorosilane and triethoxychlorosilane.

Hyde and De Long (96) treated diphenyldichlorosilane with ethanol, obtaining diphenyldiethoxysilane.

Y. N. Vol'nov (304) has prepared various tetraalkoxysilanes with halogens in the alkyl group.   By the action of 1,3-dichloropropanol-2 on tetrachlorosilane Vol'nov formed compounds of the formula $ROSiCl_3$, $(RO)_2SiCl_2$, $(RO)_3SiCl$ and $(RO)_4Si$, where R was $(CH_2Cl)_2CHO$—.   A comparison of the relative amounts of each formed with different proportions of reactants is interesting.

In the same manner Vol'nov prepared $CH_2BrCHBrCH_2OSiCl_3$ and $(CH_2BrCHBrCH_2O)_2SiCl_2$.   The latter proved quite unstable, decomposing even at 1 mm. pressure when distilled.

Andrianov (222) treated tetrachlorosilane with methyl, ethyl, butyl and *i*-butyl alcohols to make the corresponding tetraalkoxysilanes in about 84 per cent yields.   The alcohols were 99 per cent anhydrous. Kalinin (305) carried out the same reaction in benzene, initiating the reaction at 0°, then heating at temperatures from 50° to 60°.   By this

method there were prepared triethoxychlorosilane, tri-*s*-butoxychlorosilane and tri-*i*-amoxychlorosilane. Each of these products was then treated with ethylmagnesium bromide and phenylmagnesium bromide with substitution of ethyl or phenyl for chlorine.

Sauer (309) prepared trimethylmethoxysilane, trimethylethoxysilane and trimethylbutoxysilane by the action of the proper alcohol on trimethylchlorosilane. Data on these products are listed in Chapter 10.

Vol'nov and Mishelevich (310) prepared high molecular weight ethers of silicon by the same general method, using thymol, guaiacol and carvacrol. An ether solution of thymol was added slowly to tetrachlorosilane and the system then warmed for thirty minutes. Different products were obtained from mixtures of different molar proportions. With a thymol/tetrachlorosilane molar ratio of 0.45/1.00, ROSiCl₃ was the product; with a ratio of 2.00/1.00, (RO)₂SiCl₂; and with 3.33/1.00, (RO)₃SiCl. Carvacrol was similarly used but in only one ratio 2.00/1.00. The major product was ROSiCl₃. Guaiacol was used first in the molar ratio of about 0.5/1.0, giving ROSiCl₃, then in the ratio of 2.00/1.00, in which (RO)₂SiCl₂ was formed.

It is interesting to note that on the distillation of diguaiacoxydichlorosilane, the distillate contained no chlorine. Instead, pyrocatechol appeared. It was finally shown that the product had decomposed to form the di-dipyrocatechoxysilane and methyl chloride:
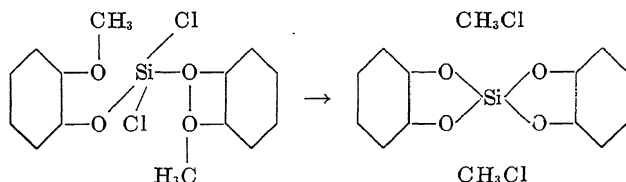
In U. S. Patent 2386793 (127) will be found descriptions of "new polymeric silicon compounds" and more especially "polysilicon esters and linear polysilicon esters." An organic group formed an integral part of the chains with carbon connected to silicon. R_2SiX_2 was allowed to react with a polyhydric alcohol or phenol. These syntheses appear very interesting and should lead to some rather useful products. Certainly the well-known stability of the carbon-silicon bond should produce a compound capable of incorporation into a multitude of commercial products of broad adaptability. In U. S. Patent 2395880 (264), also from the Du Pont laboratories, "polysilicic acid" was first prepared by the acidification of sodium silicate. Esterification could then be brought about by addition of the esterifying agent and abstraction of water, or the water could be

taken out first and the anhydrous acid esterified directly. The ratio of alkyl to silicon should be kept between 0.05/1.00 and 2.00/1.00.

Peppard, Brown and Johnson of the University of Chicago (128, 129, 130, 131) have presented a wealth of data regarding the physical and chemical properties of polyalkoxysilanes and definite experimental directions in connection with the determination of these properties as well as with the syntheses themselves.

In reference 128, alkoxychlorosilanes prepared by the action of the appropriate dry alcohol on tetrachlorosilane were discussed. These compounds were made, then alcoholyzed with some alcohol, generally different from the one used in the first place. In all, thirty-seven compounds were prepared and reported. The experimental details are easy to follow. Different procedures of water hydrolysis then led to (a) disiloxanes or to (b) oxosilanes, the latter viscous liquids.

In the second paper (129) alcoholysis of tetraalkoxysilanes was reported, usually of sufficiently high velocity in itself, as was the case when using cyclohexyl, s-butyl or crotyl alcohols or ethylene glycol. In some cases dry hydrogen chloride or tetrachlorosilane in small amounts had to be used. Aqueous hydrochloric acid was not satisfactory owing to its tendency to form polysiloxanes.

In the third contribution (130) the reactions involved replacement of ethoxyl by fluorine and further conversions:

$$SbF_3 + 2Si(OC_2H_5)_4(SbCl_5) \rightarrow FSi(OC_2H_5)_3 + F_2Si(OC_2H_5)_2 + Sb(OC_2H_5)_3$$
$$FSi(OC_2H_5)_3 + 3C_4H_9OH \rightarrow FSi(OC_4H_9)_3 + 3C_2H_5OH$$
$$FSi(OC_2H_5)_3 + 3CH_2{=}CHCH_2OH \rightarrow FSi(OCH_2CH{=}CH_2)_3 + 3C_2H_5OH$$
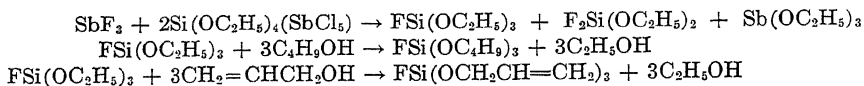
Then, in reference 131, additional methods were described for radical interchange or transesterification. Satisfactory catalysts were aluminum chloride, aluminum ethoxide, antimony ethoxide and similar products. The rate of radical interchange between tetramethoxysilane and the ester of a carboxylic acid seemed quite definitely determined by the nature of the acid. For instance, ethyl formate reacted most readily, ethyl acetate second, followed by ethyl butyrate and diethyl carbonate in that order. Tetraethoxysilane and tetrabutoxysilane did not interchange radicals after long heating, at least not to any appreciable extent; but the reaction went to statistical completion in 4.5 hours in the presence of magnesium aluminum ethoxide. The interchange between tetraethoxysilane and tetraalloxysilane was also studied.

Sauer (132) has contributed the results of work on the treatment of certain halogen-substituted silanes with aliphatic alcohols:

$$(CH_3)_2SiCl_2 + 2C_4H_9OH \rightarrow 2HCl + (CH_3)_2Si(OC_4H_9)_2$$
$$CH_3SiCl_3 + 3C_4H_9OH \rightarrow 3HCl + CH_3Si(OC_4H_9)_3$$
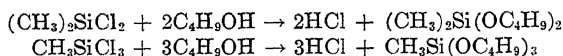
The yield of dimethyldibutoxysilane amounted only to 67 per cent, based on the amount of dimethyldichlorosilane at the beginning of the reaction. As a test, the product was boiled with benzoyl chloride according to Ladenburg's reaction (66):

$$(CH_3)_2Si(OC_4H_9)_2 + 2(C_6H_5)COCl \rightarrow (CH_3)_2SiCl_2 + 2C_6H_5COOC_4H_9$$
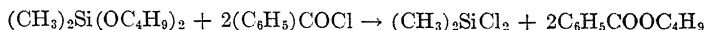
Also, from this reaction there was isolated 1,1,3,3-tetramethyl-1,3-dibutoxydisiloxane, formed when dimethyldibutoxysilane was allowed to stand nine months. Butyl alcohol was isolated as a by-product; consequently it was assumed that hydrolysis had taken place:

$$2(CH_3)_2Si(OC_4H_9)_2 + 2HOH \rightarrow 2C_4H_9OH + 2(CH_3)_2Si(OC_4H_9)OH$$
$$2(CH_3)_2Si(OC_4H_9)OH \rightarrow HOH + ((CH_3)_2Si(OC_4H_9))_2O$$
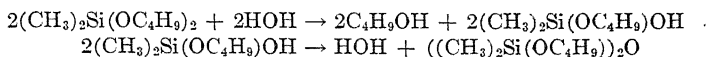
It was noticed that spontaneous refluxing ceased after a certain definite amount of butanol had been added to dimethyldichlorosilane. This seemed to indicate that one chlorine was more easily moved than the other. A reaction carried out with just this amount of butanol gave a good yield of dimethylbutoxychlorosilane.

Neutral hydrolysis of dimethyldibutoxysilane in water, dioxane and butanol, gave, in addition to unreacted material, 1,1,3,3-tetramethyl-1,3-dibutoxydisiloxane and 1,1,3,3,5,5-hexamethyl-1,5-dibutoxytrisiloxane.

Pittsburgh Plate Glass Co. (134) has patented the formation of certain unsaturated polyalkoxysilanes (U. S. Patent 2394642).

It might be pointed out that not all simple olefinic alcohols are easily handled. For instance in paragraph 2 of the above patent, (U. S. 2394642) are listed many alcohols with double bonds in their molecules. Almost all these have the double bonds between the second and third carbons, counting from the hydroxyl, or even farther away. There is a possibility, however, that "isopropenyl" alcohol might be $CH_2{=}C(CH_3)OH$. This alcohol might be stable in its compounds if not in a free state. It would be interesting to know just how the silicon derivatives of this alcohol could be prepared. The alcohol is, of course, the enol form of acetone and the sodium salt of this enol form can easily be made. Comparative data on the relative stability of Si-O-C bonds and Si-C bonds would be desirable, especially with respect to compounds such as $(C_2H_5O)_3SiOCH_2CH_2OSi(OC_2H_5)_3$.

It would appear that complete polymerization of certain compounds resulted in liquids and that less complete in some cases gave solids. This is not without parallel. The reaction or reactions covered in example 3 deserve more detailed study. Undoubtedly disproportionation helped

set up the composition of the final mixture.   In examples 4 and 5 no mention was made as to whether the final product contained as much chlorine as the reactants.   Did the polymerization take place entirely on the allyl section or was there some hydrolysis of the chlorines?

The American Stove Co. (526) has patented the treatment of oxychlorosilanes with two parts by weight of phenol with gradual heating to 850°F. Hydrogen chloride was evolved, and above 400° phenoxysilanes boiled away and were collected.   Phenoxy compounds were obtained with as many as seven silicon atoms per molecule, of the general formula $Si_nO_{n-1}(OC_6H_5)_{2n+2}$.

A German patent (327) dated 1943 described the formation of a hydrolysis product of "silicon chloroformate" suitable for use as "wettable silicon formate anhydride."

Tetraethoxysilane has been found to react with methacrylic acid to form ethanol and triethoxysilicyl methacrylate (456).

Dow Chemical Co. (515, 518) has covered the production of certain high molecular weight compounds of the general formula $RCOOSiR'_3$ and $RCOOSi(OR')_3$ and their hydrolysis to polymerized materials.

Schuyler, Weaver and Reid (583) have prepared various substituted silicyl esters of acetic acid by interaction of tetrachlorosilane or other silicon compound and sodium acetate.   Thus there were synthesized $Si(OOCCH_3)_4$, $CH_3Si(OOCCH_3)_3$, $CH_3SiH(OOCCH_3)_2$, $(CH_3)_2Si(OOCCH_3)_2$, $(CH_3)_3SiOOCCH_3$, $C_2H_5Si(OOCCH_3)_3$, $(C_2H_5)_2Si(OOCCH_3)_2$, $iC_3H_7Si(OOCCH_3)_3$, $(iC_5H_{11}O)_3SiOOCCH_3$.   Yields ranged between 35.8 and 64.3 per cent.

Recently, Abrahamson, Joffe and Post (641) have found that absolute ethyl alcohol will react with hexachlorodisiloxane to form hexaethoxydisiloxane.   Absolute propyl and butyl alcohols reacted similarly.   Hexachlorodisilane reacted with absolute ethyl and propyl alcohols to form hexaethoxydisilane and hexapropoxydisilane, respectively.   The interaction of hexachlorodisiloxane and ethyl alcohol unfortunately did not produce nearly as much of the expected product as of tetraethoxysilane. This turn of affairs, however, introduced an interesting complication at least.   When propyl and butyl alcohols were allowed to react with hexachlorodisiloxane, about a 1/1 ratio existed between the weight of expected product and the corresponding tetraalkoxysilane.   Tetraethoxysilane was also formed when ethyl alcohol reacted with hexachlorodisilane, and the same difficulty was experienced using propyl alcohol.   This tendency to form tetraalkoxysilanes under these conditions is being investigated further.

Friedel and Crafts (554) heated at 160° and in a closed vessel three moles of tetraethoxysilane and one of tetrachlorosilane with formation of triethoxychlorosilane (b.p. 155°–157°).   Diethoxydichlorosilane was also

isolated (b.p. 136°). Triethoxychlorosilane reacted with amyl alcohol to form triethoxyamoxysilane (b.p. 216°–225°). In 1865 the same investigators (558) reported interaction of methyl alcohol and tetraethoxysilane to form dimethoxydiethoxysilane. Methanol and tetrachlorosilane gave some hexamethoxydisiloxane, in addition to tetramethoxysilane.

German interests in 1916 patented as U. S. Patent 1178731 (344) the action of a high molecular weight polyfunctional alcohol on tetraethoxysilane with the formation of silicon ethers of the higher alcohol. At about the same time, similar reactions and processes were patented in Germany (424).

U. S. Patent 2048799 (300) was issued to E. I. du Pont de Nemours and Co.; in 1936, covering "Silicon Esters of Modified Polyhydroxy Alcohols."

In this patent, tetraethoxysilane was treated with polyhydroxy alcohols such as glycerin, modified by having one hydroxyl group converted to —OR. R could be an aliphatic or aromatic carboxylic acid radical, or an aliphatic, aromatic or aliphatic-aromatic hydrocarbon radical.

The two reactants were heated to gentle boiling for periods of from six to eight hours. Tetraethoxysilane was used because of its ready availability, and ease of removal and recapture of ethanol. Thus were used glyceryl ethyl ether, glyceryl mono acetate and glycerin esterified with one equivalent of linseed oil. Cottonseed oil may be substituted for linseed. With any of these radicals present which are unsaturated, there is an obvious opportunity to polymerize on the acid section of the compound. Certain resins could also be used in place of the glyceryl esters or ethers, resins prepared by the action of polybasic acids on glycerin.

Klein and Nienburg (301) carried out some rather interesting synthetic work on radical interchange between tetraethoxysilane and certain glycerides. Their purpose was biochemical in character—the preparation of lipoid-like compounds of novel properties especially with respect to susceptibility to hydrolysis, absorption, proliferation and resistivity. The reactants were heated in molar proportions for complete reaction, in a sealed tube or autoclave, at temperatures between 150° and 160°. Products were of the nature of:

$$\left[\begin{array}{l} CH_2OOCR \\ | \\ CHOOCR \\ | \\ CH_2O \end{array} \right.\cdots\cdots \Big]_4 ---Si \quad \text{and} \quad \left[\begin{array}{l} CH_2OOCR \\ | \\ CHOH \\ | \\ CH_2O \end{array} \right.\cdots\cdots \Big]_4 ---Si$$
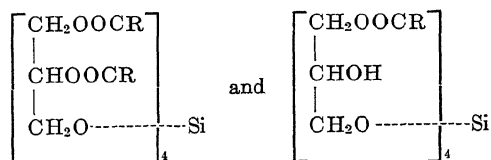
Excess of tetraethoxysilane did not affect the character of the products. Apparently the remaining acyl groups did not react. Thus there were prepared:

$$\left[\begin{array}{l} CH_2OOCC_{17}H_{35} \\ CHOOCC_{17}H_{35} \\ CH_2O\text{------}Si \end{array}\right]_4 \qquad \left[\begin{array}{l} CH_2OOCC_3H_7 \\ CHOOCC_3H_7 \\ CH_2O\text{------}Si \end{array}\right]_4$$

$$\left[\begin{array}{l} CH_2OOCC_{17}H_{35} \\ CHOH \\ CH_2O\text{------}Si \end{array}\right]_4 \quad \left[\begin{array}{l} CH_2OOCC_{17}H_{33} \\ CHOH \\ CH_2O\text{------}Si \end{array}\right]_4 \quad \left[\begin{array}{l} CH_2OOCC_3H_7 \\ CHOH \\ CH_2O\text{------}Si \end{array}\right]_4$$
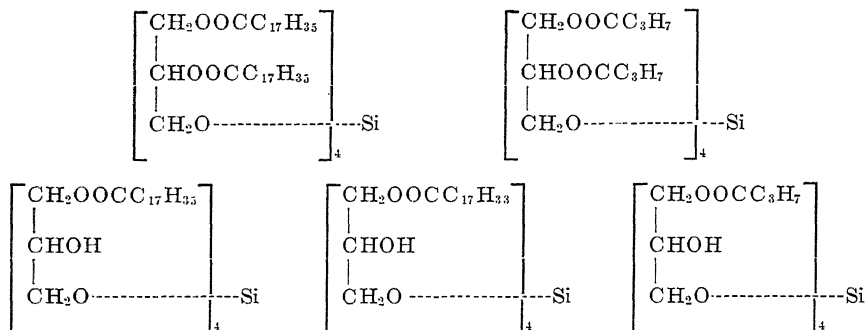
The by-product in each case was ethanol.

A novel series of tetraalkoxyl derivatives of silane was patented by the German I.G. (302) in 1937. These polyethers were prepared by treating tetraethoxysilane with monohydroxyalkyl amines in water. For instance, monoethanol amine reacted with tetraethoxysilane to form tetra-β-aminoethoxysilane. The products were expected to have pharmaceutical value.

Byk-Guldenwerke (303) patented other derivatives of the same nature. By interaction of tetraethoxysilane or tetrapropoxysilane with the proper high molecular weight alcohol, there was obtained a series of compounds:

$$C_{16}H_{33}OSi(OC_2H_5)_3$$
$$(C_{16}H_{33}O)_2Si(OC_2H_5)_2$$
$$(C_{20}H_{38}O_3)_2Si(OC_2H_5)_2 \quad \text{from ethyl ricinoleate}$$
$$C_{10}H_{19}OSi(OC_2H_5)_3 \quad \text{from menthol}$$
$$(C_{10}H_{19}O)_2Si(OC_2H_5)_2 \quad \text{from menthol}$$
$$C_5H_9O_3Si(OC_2H_5)_3 \quad \text{from ethyl lactate}$$
$$(C_5H_9O_3)_2Si(OC_2H_5)_2 \quad \text{from ethyl lactate}$$
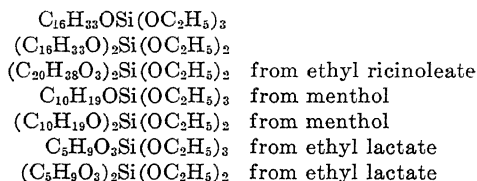
This was a continuation of German Patent 625077 (360).

In 1947, Kreshkov (646) reported attempts to form similar compounds by the action of tetrachlorosilane and of tetraethoxysilane on hydroxyacids and their methyl esters. Tetrachlorosilane resulted in dehydration, with addition of silicon compound to the double bond. After hydrolysis there were formed compounds of the type R—CHCl—CH(R)—SiOOH. These proved to be viscous materials, incapable of distillation. So also were those compounds resulting from the action of tetraethoxysilane on the free hydroxyacids. Silicic acid was formed here. But the methyl esters reacted with tetraethoxysilane to form compounds or mixtures which were distillable at low pressures and above 250°. Full details will be found in *Chemical Abstracts*.

U. S. Patent 2399697 (376), dated May 7, 1946, covers a most interesting and probably practical type of reaction. To quote from the example,

20 gallons of soybean oil was treated with 5 ounces of tetrachlorosilane under positive pressure exerted by carbon dioxide at 100° for 6 hours. This pressure, 30 to 75 pounds, was released after a time, whereupon quantities of HCl were evolved. Obviously, alcoholic hydroxyls in the soybean oil had reacted with tetrachlorosilane to form C—O—Si linkages. Since more than one of these linkages was undoubtedly present on each silicon atom, cross linkages were thereby set up between linear acid radicals of the oil, thereby binding polymerized units together in higher three-dimensional polymers. The statement that chlorine gas may be used for the purpose does not admit of easy explanation on this basis, however. Polymerization was completed through the action of benzoyl peroxide under heat and pressure.

An overall explanation of the reactions involved might follow the lines suggested in claim 1 of the patent. It is stated here that the reaction might be one of chlorination, irrespective of the agent used. The resulting products may be said to be more unsaturated and therefore more susceptible to further polymerization.

Almost as a continuation of the foregoing, investigators at government laboratories (447) have prepared compounds of high molecular weight by the interaction of tetraethoxysilane with stearyl alcohol, oleyl alcohol, linoleyl alcohol and similar compounds from soybean and linseed oils. Films made from these polyethers and dried by exposure gradually became tacky and decomposed. When baked, the tetraethers became hard, showing good resistance to cold water, hot water and cold dilute alkalies. The tendency to decompose on exposure was, in general, low.

There are many other methods for the preparation of silicon ethers. Kipping in 1944 (54) prepared a dicyclic compound with oxygen between silicon and carbon, with the following structure:

$$(C_6H_5)_2C—O \qquad O—C(C_6H_5)_2$$
$$\diagdown \qquad \diagup$$
$$Si$$
$$\diagup \qquad \diagdown$$
$$(C_6H_5)_2C—O \qquad O—C(C_6H_5)_2$$
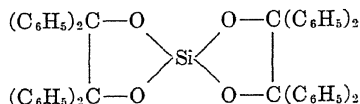
U. S. Patent 2381137 (116) covers the preparation of tetrachloroethoxysilane by the action of ethylene oxide on tetrachlorosilane. Thus the evolution of hydrogen chloride was avoided. The little hydrogen chloride which is usually present in tetrachlorosilane acted merely as a catalyst for the major reaction. This seemed to bring good results.

In U. S. Patent 2381138 (119), the claims of 2381137 were expanded to cover compounds of the type in which one or more alkyl radicals are found attached to the same atom of silicon which holds, in addition, one or more halogenated alkoxyl groups. The difference in synthesis as compared with U. S. Patent 2381137 lay in the fact that here, for instance in Example

1, use was made of methyltrichlorosilane and ethylene oxide instead of tetrachlorosilane. Likewise, Example 2 used trimethylchlorosilane and Example 3 a mixture of methyldichlorosilane, trichlorosilane, and tetrachlorosilane. The three expected products were obtained here but yields were not mentioned. This is to be deplored, since some hint would be appreciated as to the relative reactivities of these three compounds in some competitive reaction under identical conditions. A mixture of tetrachlorosilane and trimethylchlorosilane in Example 4 formed six products.

U. S. Patent 2381139 (120) described azeotropic mixtures of various methylchlorosilanes and their separation.

Sauer and Patnode (355) have prepared eight chloroalkoxysilanes by the action of ethylene oxide on various selected substituted silanes (see reference 116). Thus by bubbling ethylene oxide through the silane there were formed $Si(OCH_2CH_2Cl)_4$, $CH_3Si(OCH_2CH_2Cl)_3$, $(CH_3)_2Si(OCH_2-CH_2Cl)_2$, and $(CH_3)_3SiOCH_2CH_2Cl$. By contact there were formed $HSi(OCH_2CH_2Cl)_3$, $C_6H_5Si(OCH_2CH_2Cl)_3$, $CH_3SiH(OCH_2CH_2Cl)_2$, $(C_6H_5)_2Si(OCH_2CH_2Cl)_2$ and $(CH_3)_3SiOCH_2CH_2Cl$. Yields ranged between 68 and 96 per cent.

In addition the chemistry of trimethyl-β-chloroethoxysilane was studied more in detail:

$$(CH_3CO)_2O + (CH_3)_3SiOCH_2CH_2Cl$$
$$\rightarrow (CH_3)_3SiOSi(CH_3)_3 + CH_3COOCH_2CH_2OSi(CH_3)_3$$
$$C_6H_5COCl + (CH_3)_3SiOCH_2CH_2Cl \rightarrow (CH_3)_3SiCl$$
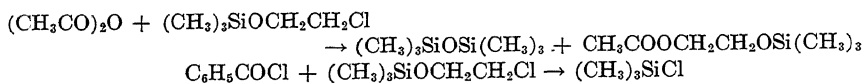
Gilliam, Meads and Sauer (435) prepared $CH_3Si(OCH_2CH_2Br)_3$ and $(CH_3)_2Si(OCH_2CH_2Br)_2$ by the action of ethylene oxide on CH_3SiBr_3 and $(CH_3)_2SiBr_2$.

Trimethylethoxysilane (124) has been found to react with phosphorus pentachloride to form trimethylchlorosilane. Gilman and Clark (504) treated ethyl sodioacetoacetate with triethylchlorosilane, obtaining ethyl β-triethylsilicylcrotonate. This compound was found to react with acetyl chloride, forming triethylchlorosilane and ethyl β-acetoxycrotonate. Ketonic hydrolysis with 10 per cent hydrochloric acid gave acetone and hexaethyldisiloxane.

Ladenburg (572) in 1871 studied the action of sodium and diethylzinc on tetraethoxysilane. Triethoxyethylsilane was the first product, then diethoxydiethylsilane. Also, acetyl chloride reacted to give ethyl acetate:

$$(C_2H_5)_2Si(OC_2H_5)_2 + CH_3COCl \rightarrow (C_2H_5)_2Si(OC_2H_5)Cl + CH_3COOC_2H_5$$
$$(C_2H_5)_2Si(OC_2H_5)Cl + CH_2COCl \rightarrow (C_2H_5)_2SiCl_2 + CH_2COOC_2H_5$$
$$(C_2H_5)_2Si(OC_2H_5)_2 + 2C_6H_5COCl \rightarrow (C_2H_5)_2SiCl_2 + 2C_6H_5COOC_2H_5$$
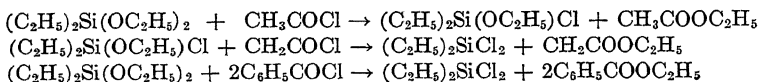
Other reactions were also investigated:

$$(C_2H_5)_2SiCl_2 + HOH \rightarrow 2HCl + (C_2H_5)_2SiO \text{ (syrup)}$$
$$(C_2H_5)_2SiO. + O_3 \rightarrow C_2H_5SiOOH$$
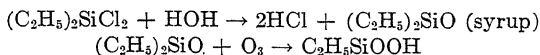
Data were presented on tetraethoxysilane, ethyltriethoxysilane, diethyldiethoxysilane, triethylethoxysilane and tetraethylsilane. Later, Ladenburg (573, 574) found that triethylhydroxysilane, formed by hydrolysis of triethylethoxysilane, reacted with acetyl chloride to give triethylchlorosilane.

Friedel and Ladenburg (65, 556) prepared ethyltriethoxysilane by the action of triethoxychlorosilane on a mixture of sodium and diethylzinc. In 1872, Ladenburg (66) prepared diethoxydiethylsilane by the action of diethylzinc on ethyltriethoxysilane. The major product, diethoxydiethylsilane, was put through several reactions including alkaline hydrolysis, treatment with acetyl chloride and acid hydrolysis with hydriodic acid:

$$2Na + Zn(C_2H_5)_2 + 2C_2H_5Si(OC_2H_5)_3 \rightarrow Zn + 2C_2H_5ONa + (C_2H_5)_2Si(OC_2H_5)_2$$
$$KOH + HOH + (C_2H_5)_2Si(OC_2H_5)_2 \rightarrow C_2H_5SiOOK + CH_3COOK + H_2$$
$$CH_3COCl + (C_2H_5)_2Si(OC_2H_5)_2 \rightarrow (C_2H_5)_2Si(OC_2H_5)Cl + CH_3COOC_2H_5$$
$$2HI + (C_2H_5)_2Si(OC_2H_5)_2 \rightarrow (C_2H_5)_2SiO + 2C_2H_5)I + HOH$$
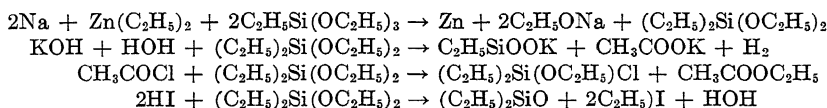
A summary of further reactions covered in this paper will be found in Chapter 3.

Corning Glass Works' U. S. Patent 2386452 (126) included the following:

$$LiC_6H_5 + Si(OC_2H_5)_4 \rightarrow C_2H_5OLi + C_6H_5Si(OC_2H_5)_3$$
$$LiC_6H_5 + CH_3Si(OC_2H_5)_3 \rightarrow C_2H_5OLi + C_6H_5Si(CH_3)(OC_2H_5)_2$$
$$LiC_6H_4N(CH_3)_2\text{-}p + Si(OC_2H_5)_4 \rightarrow C_2H_5OLi + p\text{-}(CH_3)_2NC_6H_4Si(OC_2H_5)_3$$
$$3LiC_6H_4N(CH_3)_2\text{-}p + Si(OC_2H_5)_4 \rightarrow 3C_2H_5OLi + [(CH_3)_2NC_6H_4]_3SiOC_2H_5$$
$$HOH + (p\text{-}(CH_3)_2NC_6H_4)_3SiOC_2H_5 \rightarrow C_2H_5OH + [p\text{-}(CH_3)_2NC_6H_4]_3SiOH$$
$$LiC_6H_4CH_3\text{-}p + Si(OC_2H_5)_4 \rightarrow C_2H_5OLi + p\text{-}CH_3C_6H_4Si(OC_2H_5)_3$$
$$LiC_6H_3(CH_3)3\text{-}2,5 + Si(OC_2H_5)_4 \rightarrow C_2H_5OLi + 2,5\text{-}(CH_3)_2C_6H_3Si(OC_2H_5)_3$$
$$p\text{-}LiC_6H_4C_6H_5 + Si(OC_2H_5)_4 \rightarrow C_2H_5OLi + p\text{-}C_6H_5C_6H_4Si(OC_2H_5)_3$$
$$LiC_6H_4NH_2\text{-}p + Si(OC_2H_5)_4 \rightarrow C_2H_5OLi + p\text{-}H_2NC_6H_4Si(OC_2H_5)_3$$
$$2LiC_6H_4CH_2OH\text{-}p + Si(OC_2H_5)_4 \rightarrow 2C_2H_5OLi + [p\text{-}HOCH_2C_6H_4]_2Si(OC_2H_5)_2$$

Yields varied between 18.1 and 28.6 per cent. Quite logically, greater efficiency was claimed for the use of lithium instead of other metals because of the greater reactivity of this element when needed, and its consequent ability to react at lower temperatures. Most of the material covered in this patent has also been described in Great Britain (508).

Gilman and Clark (449) have reported preparation of tetraethylsilane by the action of ethyllithium on tetraethoxysilane. *i*-Propyllithium (522) caused the replacement of only three ethoxyl groups. Gilman and Vernon (563) were unsuccessful in attempts to bring about a reaction between tetra-*p*-toloxysilane and phenylmagnesium bromide.

Kipping (51) also prepared dicyclohexylcyclohexoxyphenylsilane by the action of cyclohexylmagnesium bromide on phenyltrichlorosilane; but in this synthesis the ether was evaporated from the Grignard mixture and the resulting system heated at 160° to 180° for three hours. This of course induced oxidation of Si—C to Si—O—C or Si—O—Si. The product melted at 103° to 104°. Hydrobromic acid converted this compound to dicyclohexyloxosilane. Acetyl chloride and benzoyl chloride reacted with dicyclohexylcyclohexoxyphenylsilane forming dicyclohexylphenylhydroxysilane.

Soviet interest in silicon syntheses through the action of the Grignard reagent has not been wanting. Vol'nov and Reutt (224) prepared triethoxyethinylsilane by the action of tetraethoxysilane on phenylethinylmagnesium bromide:

$$C_6H_5C\equiv CMgBr + Si(OC_2H_5)_4 \rightarrow C_2H_5OMgBr + C_6H_5C\equiv CSi(OC_2H_5)_3$$
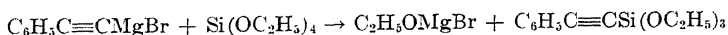
in yields of 75 per cent.

The alkylation of esters, or the substitution of alkyl for alkoxyl, is covered in U. S. Patent 2380057 (255), specifically in connection with tetraethoxysilane by action of the Grignard reagent. The object of the work was to replace two alkoxyl groups attached to the same silicon by two alkyls. The process was very efficiently carried out by pumping methyl chloride gas into a tight flask containing magnesium and tetraethoxysilane. A little ethyl bromide or iodine was necessary to start the reaction, as chlorides do not form Grignard reagents as easily as bromides. The statement was made that formation of $R_2Si(OR')_2$ is only possible in good yields when the Grignard reagent is prepared "*in situ*" or "is nascent."

Ethyl chloride also reacted satisfactorily, but separation of products was quite difficult owing to the slight difference in boiling points. Butyl and amyl chlorides were also used. In the case of the methyl derivative, $(CH_3)_2Si(OC_2H_5)_2$ and $CH_3Si(OC_2H_5)_3$ were formed in the ratio of 2/1.

Corning Glass Works' U. S. Patent 2384384 (122) includes directions for the preparation of pure dimethyldiethoxysilane by the use of "nascent" Grignard reagents. In U. S. Patent 2386441 (371) the preparation of trimethylethoxysilane and its hydrolysis are discussed. Water, acidified with hydrochloric acid converts the ethoxyl group to hydroxyl; then on standing, loss of water causes the formation of hexamethyldisiloxane, b.p. 99° (760 mm). This was followed by U. S. Patent 2390518 (373) from the same laboratories covering the following reaction:

$$CH_3MgCl + (CH_3)_2Si(OC_2H_5)_2 \rightarrow (CH_3)_3SiOC_2H_5 + C_2H_5OMgCl$$
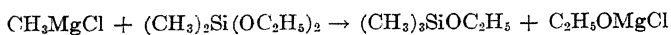
Whitmore and co-workers (361) treated tetraethoxysilane with ethylmagnesium bromide, forming ethoxytriethylsilane. This compound was

hydrolyzed and dehydrated in acid solution to hexamethyldisiloxane, and then allowed to react with sulfuric acid and ammonium chloride to form triethylchlorosilane.

The British Thomson-Houston Co., (647) has patented the preparation of compounds of the type $Si(OR)_4$ by the high temperature interaction of silicon and alcohols.

Hackford, Shaw and Smith (648), British Patent 591149 (1947) have described the treatment of tetraethoxysilane with Grignard reagents forming, after hydrolysis, resinous materials.

Whitmore and associates (653) have prepared trimethylethoxysilane by the action of methylmagnesium bromide on tetraethoxysilane.

R. N. Meals (362) treated triethylsilane with lithium ethoxide forming ethoxytriethylsilane in 74 per cent yield.

Dolgov and Vol'nov (552) in the course of extensive hydrogenations reported that tetraethylsilane formed ethane and hexaethyldisilane, while tetraethoxysilane went over to orthosilicic acid and ethylene at 250°, at which temperature tetraethylsilane is stable. Tetraphenoxysilane begins to decompose at 280° and is 100 per cent reacted at 380°. The products and phenol and silicon. Tetra-*p*-toloxysilane gave some silica. Tetraethoxysilane, heated for 25 hours at 200° and at 100 atmospheres, formed ethanol and hexaethoxydisilane. Tetra-*i*-amoxysilane went over to *i*-amyl alcohol and hexa-*i*-amoxydisilane, while tetracyclohexoxysilane gave a quantitative yield of silica and cyclohexene.

In 1939, Andrianov (532) reported the hydrolysis of compounds such as $RSi(OC_2H_5)_3$ leading to a mixture of siloxanes—gum-like resins soluble in organic solvents. The solutions formed films. Their elastic properties were capable of modification by the action of plasticizers.

Corning Glass Works holds U. S. Patent 2371050 (113) which covers the water hydrolysis of dimethyldiethoxysilane. The product was dimethyldihydroxysilane, which immediately dehydrated and polymerized when heated. The hydrolysis of a mixture of dimethyldiethoxysilane and ethylphenyldichlorosilane was described by Corning Glass Works in U. S. Patent 2377689 (343). Other mixtures comprised dimethyldiethoxysilane and ethyltriethoxysilane, dimethylphenylethoxysilane and methyltriethoxysilane, phenyltrichlorosilane and ethoxytrimethylsilane, and diethyldichlorosilane and ethylphenyldichlorosilane. The hydrolysis of pure dimethylphenylethoxysilane was also discussed. Another patent (370) covered the preparation of a polymeric silicone by the hydrolysis of dimethyldiethoxysilane and methyltriethoxysilane. Thus, hydrolysis with $2N$ hydrochloric acid (Example 1) at temperatures less than 45° produced an oil with a viscosity of "70 Saybolt seconds at 86° F." The polymers can be used as pressure fluids.

"Ethyl Silicate 40" (283) is a product of the laboratories of Carbide and Carbon Chemicals Corporation with the following properties:

Specific gravity (20°/20°)	1.050 to 1.070
Boiling point (760mm) Range	Below 80° none
	Below 110° less than 5%
Available silica by weight	38% to 42%
Maximum acidity as HCl by weight	0.10%
Flash point (open cup)	90°F.

To quote the commercial literature (283), this product is a mixture of polymerized tetraethoxysilanes. The formula is given as

$$(C_2H_5O)_3Si-O-\overset{\displaystyle OC_2H_5}{\underset{\displaystyle OC_2H_5}{\overset{|}{\underset{|}{Si}}}}-O-Si\overset{\displaystyle OSi(OC_2H_5)_3}{\underset{\displaystyle OSi(OC_2H_5)_3}{<}}OC_2H_5$$
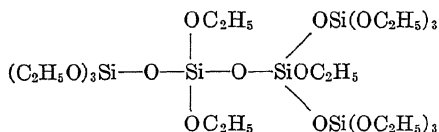
This compound is capable of undergoing hydrolysis. All ethoxyls are thereby replaced by hydroxyls. The probability that a compound of this type would form had already been indicated, as a matter of fact (284). Carbide and Carbon Chemicals Corp. has also described methods of hydrolysis in more definite terms (445). An additional discussion (586) of "Ethyl Silicate 40" and similar compounds has recently appeared in *Industrial and Engineering Chemistry*.

Corning Glass Works' U. S. Patent 2397895 (269) covers an improved method of hydrolysis. Heated methyl silicones with a CH_3/Si ratio of 2.5/1 were condensed and hydrolyzed with trimethylethoxysilane and water. The products were found to be more stable and viscous than those made from the concurrent hydrolysis and hardening of like substances. For instance, a mixture of 90 per cent dimethyldiethoxysilane and 10 per cent methyltriethoxysilane proved quite satisfactory.

Louise Holzapfel (335) reported physical constants for tetramethylsilane and tetraethylsilane, and then proceeded to demonstrate the presence (334) of tetracholesteroxysilane and homologs in silicotic lungs. Holzapfel and Kerner-Esser (332) found evidence for the existence of silicon compounds, presumed to be polyalkoxysilanes, in steer's blood. These compounds could be extracted with alcohol but not with ether. Tetraalkoxy silanes should be soluble in ether, at least to the extent that would have been possible here with the small amount at the disposal of the workers.

Three papers of interest to crystallographers appeared in 1942 from Dutch sources (306, 307, 308). In the first of these (306) Backer and Klasens reported preparation of 22 polyalkoxides and polymercaptides of

silane, principally for the purpose of studying their crystal structures. For instance, tri-*t*-butylmercaptochlorosilane crystallized in optically uniaxial crystals, hexa-*t*-butylmercaptodisiloxane in triclinic crystals, di-*t*-butylmercaptodi-*i*-propylmercaptosilane in the rhombic form, and hexa-*t*-butoxydisilane in hexagonal tablets. Both tri-*t*-butylmercapto-amylmercaptosilane and tri-*t*-butylmercaptocyclopentylmercaptosilane were tetragonal. Three others (307) were also found to be tetragonal, namely tetra-*t*-butylmercaptosilane, tri-*t*-butylmercapto-*s*-butylmercapto-silane and tri-*t*-butylmercapto-*t*-amylmercaptosilane.

In the third of these papers (308) tetrachlorosilane was allowed to react with selenophenol forming tetraphenylselenosilane (rhombic needles):

$$4C_6H_5SeH + SiCl_4(in\ C_6H_6) \rightarrow 4HCl + Si(SeC_6H_5)_4$$
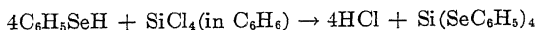
Other compounds of this type were also prepared:

$$4p\text{-}CH_3C_6H_4SeH + 8Na + SiCl_4 \rightarrow Si(SeC_6H_4CH_3\text{-}p)_4 + 8NaCl$$
$$4p\text{-}t\text{-}C_4H_9C_6H_4SeH + 8Na + SiCl_4 \rightarrow Si(SeC_6H_4C_4H_9\text{-}p)_4 + 8NaCl$$
$$4p\text{-}ClC_6H_4SeH + 8Na + SiCl_4 \rightarrow Si(SeC_6H_4Cl\text{-}p)_4 + 8NaCl$$
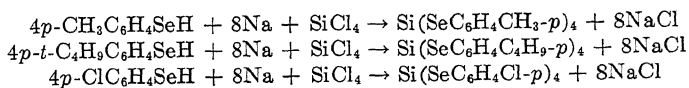
The last product crystallized in tetragonal needles.

Holzapfel, Kerner and Neuhaus (328) have studied silicon glasses whose composition lay midway between the organic and the inorganic. Products with tetraethoxysilane incorporated in their structures were liquid at room temperatures and could be "worked." The dipole character of certain nitrogen compounds was assumed to influence the rate of solidification. Under the same conditions relative times required for comparable solidification using these nitrogenous catalysts were:

p-phenylene diamine	2
p-aminophenol	3
m-phenylene diamine	6
o-phenylene diamine	10
pyridine	14
aniline	44

Hydroquinone accelerated solidification, as did other polyphenols such as resorcinol and pyrocatechol. It was stated that other influences must also be at work here in addition to dipole tendencies. Holzapfel (333) also reported data on the influence of polyalcohols on the saponification and polymerization of tetraethoxysilane and tetramethoxysilane. The rate varied as the number of hydroxyls in the catalyzing molecule; and for substituted phenols, para exerted the greatest effect, followed by meta, then ortho.

Physical properties of silicon polyethers have also been studied.

In 1909, Khotinsky (411) took occasion to correct certain figures which

had already been presented from his own laboratories. It seems that Melzer (78) in 1908 had reported the melting point of α-naphthyloxohydroxysilane as 125° to 130°, while Khotinsky and Seregenkoff (412) gave 239°. To clear up this divergence of results Khotinsky repeated the preparation of this acid, by first preparing α-naphthyltriethoxysilane and then hydrolyzing this polyether with hydriodic acid. The melting point of the final acid was 138°.

Corning Glass Works (369) has described certain molding powders and other polymers.

Imperial Chemical Industries, Ltd. (268) has covered in U. S. Patent 2396692 the polymerization of tetraalkoxysilanes to solid products by heat. One or more of these radicals must be olefinic in character. Thus tetramethalloxysilane, when heated at 250° for 40 hours in an evacuated sealed tube formed a clear, hard, transparent solid. This product was scratch-resistant, insoluble in all solvents, and infusible below 300°. Benzoyl peroxide to the extent of 0.5 per cent reduced the time of heating to 25 hours. Tetraalloxysilane also proved satisfactory.

Corning Glass Works (265) has covered certain molding powders in the British field by means of British Patent 563995. The powder was made by pulverizing a thermoplastic heat-convertible solid hydrolysis product of a hydrolyzable compound of the type $RSiX_3$, either alone or mixed with another of the type R_2SiX_2, mixing the product with a small amount of boric oxide. Organic radicals satisfactory for use as R include methyl, ethyl, propyl and phenyl. X may be halogen or ethoxyl.

Du Pont's U. S. Patent 2395550 (358) covers "Modified Alkyd Resins." Adequate criticism of this patent would be difficult. Certainly the combination of polymerizable materials is ingenious and should produce not one but a series of interesting and useful polymers.

Hunter, Warrick, Hyde and Currie (427) have reached the conclusion that certain properties of dimethylsiloxane, as compared with those of hydrocarbons and tetraalkylsilanes, "seem to depend in large part on the ionic character of the silicon oxygen bond." Thus the above generalization is applied to compounds of the type $(CH_3)_3SiO—[—Si(CH_3)_2O—]_n$ $Si(CH_3)_3$. These were prepared by the co-hydrolysis of ethoxytrimethylsilane and diethoxydimethylsilane. Considerable space in this paper was devoted to tables of data, especially of a comparative nature.

Goodwin and others (707) allowed metallic sodium to react with a chlorinated silicon ether with the following results:

$$2Na + (CH_3)_3SiCl + C_2H_5OSi(CH_3)_2CH_2Cl \rightarrow$$
$$2NaCl + (CH_3)_3SiCH_2Si(CH_3)_2OC_2H_5$$
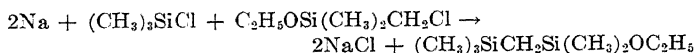
With a chlorine in place of ethoxyl the reaction was so rapid that polymers were obtained. Toluene was the solvent.

From the Du Pont laboratories (590) has come a description of the preparation of a low molecular weight silicic acid by the acidification of sodium metasilicate, which could then be transferred from the aqueous solution to butyl alcohol. Partial esterification then set in, aided by dehydration through the formation of an azeotropic distillate. There were 0.5 to 0.6 butoxyl group in these molecules for each silicon atom. The compounds appeared as resinous solids, soluble in organic solvents, and quite stable. Increase in the degree of esterification set up a corresponding increase in degree of compatibility with hydrocarbon solvents, such as chloroform, acetone and benzene. Less completely esterified esters were precipitated by benzene. Preliminary studies in viscosity showed that the molecules may be spheroidal.

Conditions were very important. Acidification of the silicate at low temperatures and rapid mixing gave a product with a final pH of 1.7, and this compound had to be transferred to butyl alcohol rather quickly before gellation set in. Extensive tables of data were given covering the physical properties of various silicic acids and esters with butoxyl/silicon ratios between 0.31 and 0.59.

A second Du Pont contribution (591) covered hydrolysis and condensation of compounds of the general type $(C_4H_9O)_xSiCl_{4-x}$. Thus were prepared $(C_4H_9O)_3SiOSi(OC_4H_9)_3$ and $[(C_4H_9O)_2SiO]_x$, where $x = 3$ to 8 inclusive. Co-polymers of butoxytrichlorosilane and dibutoxydichlorosilane gave solid resins. Liquid cyclic polymers possessed high thermal stability and little change of viscosity with temperature.

Physical properties other than those just mentioned also varied with the butoxyl content as in the case of the methyl polymers. Extensive tables of data were presented to cover conditions of hydrolysis and resultant physical properties. In the presence of sodium butoxide and at 230°, butoxysilanes suddenly gelled to highly viscous, foamy solids. Tetrabutoxysilane was the only compound isolated from these products.

Four patents from the same sources were also concerned with the preparation and properties of silicic acid sols and similar compositions.

The first of these (620) describes the preparation of a silicic acid sol made by a form of combination of silicic acid with "an organic hydrogen bonding donor compound which contains at least one oxygen atom bonded to a carbon atom..." Reactant sols of silicic acid were prepared from both sodium metasilicate and tetraethoxysilane.

The second patent of this group (621) covers a process "for improving the stability against jelling of a polysilicic acid solution." Esters of phosphoric acid were used.

The third patent (622) describes preparation of "a liquid alcohol-polysilicic acid complex" with a pH below 3.0. The process disclosed in this claim comprises mixing an aqueous polysilicic acid solution with "a

liquid alcohol having at least two carbon atoms per hydroxyl." Propanol-1 was mentioned in Example 1, propanol-2 in Example 2, and tertiary butyl alcohol in Examples 3 and 4. The reader should also be referred to previous work by Grimaux (629).

The fourth patent (635), which was actually the first chronologically, is of the same general type.

Schwerin (634) has patented and assigned to Elektroosmose A.G., a process for the preparation of "chemically pure soluble silicic acid." The process involves electrolysis of an alkali silicate solution of between 5 and 10 per cent strength. Ten years later, in 1925, the National Benzol Association of London (636) also patented in the United States a method for hydrolyzing tetrachlorosilane by water to a suitable gel and preparing an adsorbent material therefrom. Collins (637) covered the same product by a process similar to that of Schwerin (634).

Silicic acid sols are used as tanning aids (639, 640, 641).

A recent Dow Chemical Co. patent (617) has described in considerable detail interesting work on the controlled hydrolysis of compounds such as dimethyldiethoxysilane. By means outlined, polysilicones were prepared, linear in nature, with two methyl groups on each silicon and with terminal silicon bonds satisfied by ethoxyl groups. Certain generalizations appearing in the patent are of especial interest. Hydrolysis and subsequent dehydration to the polysiloxane could be accomplished through the catalytic action of sodium hydroxide, but this agent was not absolutely necessary. Water was found to be quite efficient. Data presented in the patent itself covered the variation in type and character of polymer with various conditions of hydrolysis and molecular proportions of reacting materials. It was found that ethyl alcohol, normally a product of the reaction, had the effect of inhibiting the formation of long polysiloxane chains.

The principle of radical interchange was made use of by Krieble and Burkhard (631) when *d*-dimethyldi-*s*-butoxysilane was allowed to disproportionate with dimethyldiethoxysilane, giving *d*-dimethyl-*s*-butoxyethoxysilane. Because the optical activity of the *s*-butoxy radical was maintained throughout this reaction, it was felt that the break had occurred between silicon and oxygen and not between carbon and oxygen. Certain cyclic siloxanes were also prepared by interaction of the appropriate glycol and $(CH_3)_2SiCl_2$, (A, D, E), or the proper compound with ethoxyl groups attached to silicon (A, B, C, D, F). The following were prepared:

$$
\text{(A)}\quad (CH_3)_2Si \underset{OCH_2CH_2O}{\overset{OCH_2CH_2O}{\big\langle}} Si(CH_3)_2
$$

(B) $(CH_3)_2Si$ $\diagup$ OCH$_2$ $\diagdown$ CH$_2$ $\diagdown$ OCH$_2$ $\diagup$

$$\text{(B)} \quad (CH_3)_2Si \underset{OCH_2}{\overset{OCH_2}{<}} \hspace{-0.5em} \underset{}{\overset{}{>}} CH_2$$

$$\text{(C)} \quad (CH_3)_2Si \underset{OCH_2CH_2}{\overset{OCH_2CH_2}{<}} \Big|$$

$$\text{(D)} \quad (CH_3)_2Si \underset{OCH_2CH_2}{\overset{OCH_2CH_2}{<}} \hspace{-0.5em} > O$$

$$\text{(E)} \quad (CH_3)_2Si \underset{OCH_2CH_2OCH_2}{\overset{OCH_2CH_2OCH_2}{<}} \Big| \quad \cdot$$

$$\text{(F)} \quad (CH_3)_2Si \underset{O}{\overset{OCH_2CH_2OCH_2CH_2O}{<}} \hspace{-1em} \underset{}{\overset{}{>}} Si(CH_3)_2$$
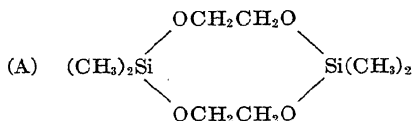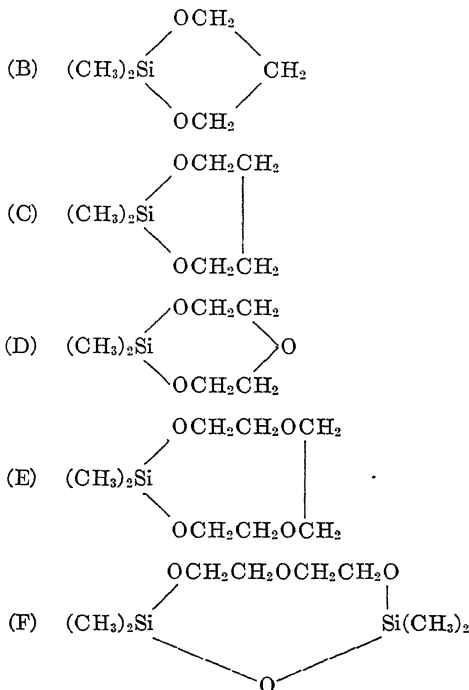
Compound A underwent polymerization easily and spontaneously to a liquid nonamer. This process was reversible when the polymer was heated at 130° to 150° at 20 mm. Polymerization seemed to be associated with a small amount of hydrolysis.

Wright and Hunter (656) studied the infra-red spectra of methyl-polysiloxanes in the range from 2 to 14 mμ. It was stated that "the great intensity of the bands involving the Si-O linkage confirms the large ionic character predicted from electronegativity difference." It was also concluded that the dipole moment of methyl attached to silicon was less than the same group attached to carbon.

Recently, Abrahamson, Joffe and Post (641) have described the preparation of certain high molecular weight polyethers of silicon. Tetra-β-methoxyethoxysilane and tetra-β-ethoxyethoxysilane were both easily prepared by interaction of tetra-ethoxysilane and methyl "Cellosolve" and ethyl "Cellosolve," respectively. The products were heavy liquids. In similar manner, phenyl "Cellosolve" reacted, but the evidence for the existence of the expected product was not as conclusive as in the first three cases.

Havill, Joffe and Post (642) have reported studies on the tendency of

hydrogen connected to silicon to react catalytically with caustic, with evolution of gaseous hydrogen. This study was intended to be of a preliminary nature and is being continued. It was first noticed that, in the preparation of triethoxysilane by the interaction of trichlorosilane and absolute ethyl alcohol, hydrogen gas was evolved when the system was allowed to warm to room temperatures (from 0°) and the resulting product was almost wholly tetraethoxysilane. Further investigation showed that this reaction, whatever it may have been, did not commence until the system had begun to warm up; furthermore, if the reaction were carried out in some non-polar solvent such as benzene, this complicating side reaction could be kept to a minimum. It was also noticed that with increasing molecular weight of the alcohol, more and more of the trialkoxysilane was formed and less of the tetra- analog. Hexaethoxydisiloxane was also isolated when ethyl alcohol was used. The evolution of hydrogen from a trialkoxysilane on treatment with caustic was studied, and this reaction was found to be nearly quantitative.

As early as 1877, Miquel (513) prepared silicon tetrathiocyanate by the action of lead thiocyanate on tetrachlorosilane. In 1906, Reynolds (514) repeated this work satisfactorily by refluxing the reactants in benzene.

Forbes and Anderson (511) in 1940 allowed tetrachlorosilane to react with silver isocyanate, obtaining a mixture of silicon cyanate and silicon isocyanate. The identities of these two compounds were shown by their hydrolysis reactions:

$$Si(NCO)_4 + 4HOH \rightarrow Si(OH)_4 + 4HNCO$$
$$Si(OCN)_4 + 12HOH \rightarrow Si(OH)_4 + 4NH_4HCO_3$$
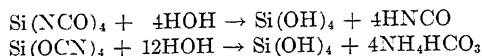
Later, Anderson (512) studied the interaction of tetrachlorosilane and silicon isocyanate and radical interchange. Rapidly at 600°, trichlorosilicyl isocyanate, dichlorosilylene diisocyanate and chlorosilylidine triisocyanate were formed from the two reactants listed above. Forbes and Anderson (510) in the same year reported that methyl alcohol, reacting with silicon tetraisocyanate, formed all four possible compounds with varying ratios of methoxyl and isocyanate and with four methoxyls per silicon.

Trichlorosilicylthiocyanate was found (497) to disproportionate, giving tetrachlorosilane and silicon tetrathiocyanate at 600° or even less. Furthermore, at 140°, after four hours of contact, tetrathiocyanatosilane, or silicon tetrathiocyanate, and the corresponding isooxygen compound also underwent radical interchange. Anderson (496) found that methyl alcohol reacted with silicon tetrathiocyanate as:

$$CH_3OH + Si(SCN)_4 \rightarrow (CH_3O)_3SiSCN$$
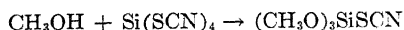
Forbes and Anderson (580) treated antimony trifluoride with silicyl isocyanate, obtaining certain volatile products and in addition tetra-

fluorosilane and antimony isocyanate. As might have been expected, all possible mixed compounds with silicon attached to varying amounts of fluorine and isocyanate were also obtained. For purposes of analysis the following reaction was carried out:

$$F_xSi(NCO)_{4-x} + (8 - x)CH_3OH \rightarrow Si(OCH_3)_4 + xHF + (4 - x)H_2NCOOCH_3$$
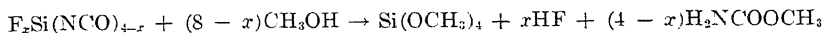
Forbes and Anderson (659) continued the work on various silicon isocyanates and isothiocyanates:

$$Cl_3SiOSiCl_3 + 6AgNCO = 6AgCl + (OCN)_3SiOSi(NCO)_3$$
$$Si(NCO)_4 + HOH = (OCN)_3SiOSi(NCO)_3 \text{ (with or without solvent)}$$
$$Cl_3SiOSi(Cl)_2OSiCl_3 + 8AgNCO = 8AgCl + (OCN)_3SiOSi(NCO)_2OSi(NCO)_3$$
$$Cl_3SiOSiCl_3 + 6AgNCS = 6AgCl + (SCN)_3SiOSi(NCS)_3$$
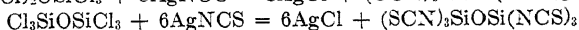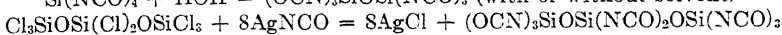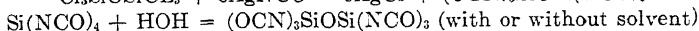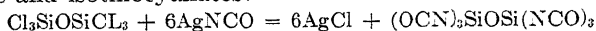
Among good solvents were mentioned acetone and 1,4-dioxane. Benzene, carbon disulfide, carbon tetrachloride and diethyl ether were of little value as solvents.

The chemistry of organic compounds with silicon attached to nitrogen overlaps the field of free radicals.

In 1873, Troost and Hautefeuille (359) treated hexaethoxydisiloxane and octaethoxycyclotetrasiloxane with ammonia. One and two ethoxyl groups were progressively replaced by amino. Tetraethoxydiaminodisiloxane could not be isolated because of its instability during purification.

In 1933, Kraus and Eatough (324) prepared the free radical, triphenylsilicyl with ethyl amine of crystallization, a stable entity melting at 45°:
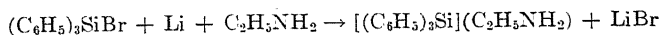
$$(C_6H_5)_3SiBr + Li + C_2H_5NH_2 \rightarrow [(C_6H_5)_3Si](C_2H_5NH_2) + LiBr$$

The reaction was carried out in ethyl amine solution and the molecular weight of the product was confirmed by determinations in benzene solution. Triphenylsilicyl with ethyl amine of crystallization added lithium to form $(C_6H_5)_3SiLi$; on standing in ether solution or, more quickly when heated, it dimerized with evolution of ethyl amine.

The reaction between tetrachlorosilane and aniline was investigated by Harden (322) in 1887. It proved to be violent and very exothermic, forming one equivalent of dianilinodichlorosilane and two of aniline hydrochloride. Water hydrolysis of the former product resulted in aniline hydrochloride and silica. In similar manner there were prepared di-o-methyl-amilinodichlorosilane, di-dimethylanilinodichlorosilane (positions of the methyls not specified) and di-α-naphthylaminodichlorosilane. Analyses of these compounds were reported but no melting points. It was found that tertiary bases formed only addition products; for example, from pyridine and quinoline came $(C_5H_5N)_2(SiCl_4)$ and $(C_9H_7N)_2(SiCl_4)$. J. E. Reynolds (323) followed this subject in the same year with a description of the interaction of thiocarbamide and tetrabromosilane in the molar ratio of 8/1. The tetrabromosilane was dissolved in dry benzene and thiocarbamide pow-

der slowly added.   There was formed an addition compound containing the two constituents in the molar ratio of 8/1.   This number, 8, for thiocarbamide was a maximum figure.   Lesser heating time resulted in a smaller number of thiocarbamide molecules for each one of tetrabromosilane, but the number never exceeded 8.   Using a larger excess of the silane, again at the boiling point of benzene but heated for twice as long, gave a product analyzing as $[CS(NH_2)_2]_8(SiBr_4)$ (C_2N_2).   In absence of air the terminal C_2N_2 did not appear.

Reynolds continued his work (320) in the following year by reporting the action of tetrabromosilane on allylthiocarbamide.   The product was an 8/1 addition product as before.   Phenylthiocarbamide reacted in the same manner.   When heated with ethanol, the 8/1 addition product formed ethyl bromide, ethyl isocyanate, tetraethoxysilane and a compound $C_4H_{20}N_9S_4Br$, reported to be

$$N \left[\begin{array}{c} H_2N \diagdown \quad \diagup SH \\ \diagup C \diagdown \\ H_2N \diagup \quad \diagdown \end{array} \right]_4^+ Br^-$$
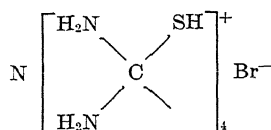
This product was shown to be identical with one made by the action of ammonium bromide on thiocarbamide.

Reynolds' third paper (317) in 1889, described the action of tetrachlorosilane on aniline in molar proportions of 1/8 in benzene.   As reported by Harden (322) the reaction was violent and exothermic, forming one equivalent of tetraanilinosilane (m.p. 137° to 138°) and four of aniline hydrochloride.   The reaction with dry hydrogen chloride was the same as reported by Harden (322).   There were also prepared, by the same method, tetra-*p*-methylanilinosilane, tetra-*o*-methylanilinosilane and tetra-*β*-naphthylaminosilane.

Kipping allowed (3) *p*-toluidine to react with benzylethylpropylchlorosilane with the formation of a product with a silicon-nitrogen linkage:

$$2 \underset{NH_2}{\bigcirc}^{CH_3} + \underset{C_2H_5}{\overset{CH_2}{\bigcirc}}C_3H_7SiCl \rightarrow \underset{NH_3Cl}{\bigcirc}^{CH_3} + \underset{C_2H_5}{\overset{CH_2}{\bigcirc}}C_3H_7SiNH\bigcirc CH_3$$
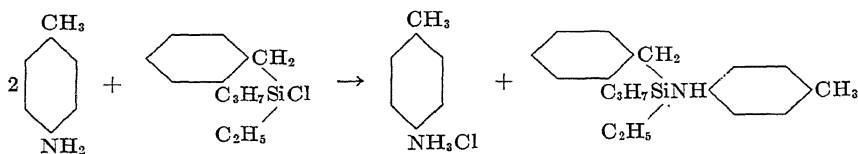
In 1921, Stock and Somieski (200) prepared trisilicyl amine by the action of chlorosilane on ammonia.

Kraus and Rosen (321), hoping to prepare the free radical triphenylsilicyl, treated triphenylchlorosilane with sodium in liquid ammonia.   However, the ammonia reacted with the chlorosilane in preference to the sodium:

$$(C_6H_5)_3SiCl + 2NH_3 \rightarrow (C_6H_5)_3SiNH_2 + NH_4Cl$$
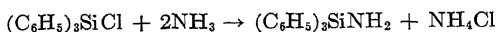
Triphenylchlorosilane was prepared by treating triphenylhydroxysilane with dry hydrogen chloride gas. It is only slightly soluble in liquid ammonia and there was therefore always an excess of sodium and of course an even greater excess of ammonia.

The actual reaction between sodium and triphenylchlorosilane was different from what was expected. From 5 to 6 equivalents of sodium per equivalent of silicon compound were used up, since the carbonsilicon bond was actually broken. Definite products were not isolable, but with four atoms of sodium to one of triphenylchlorosilane, products were found which were readily oxidizable.

Kraus and Nelson (85) prepared di-triethylsilicyl amine by the action of triethylsilane on potassium amide, and Emeleus and Miller (312, 313) treated chlorosilane with methyl amine and with ethyl amine, obtaining respectively disilyl methyl amine and disilyl ethyl amine.

Sauer (309) hydrolyzed hexamethyldisilazine, obtaining trimethylhydroxysilane:

$$2(CH_3)_3SiCl + 3NH_3 \rightarrow (CH_3)_3SiNHSi(CH_3)_3 + 2NH_4Cl$$
$$(CH_3)_3SiNHSi(CH_3)_3 + 2HOH + HCl \rightarrow 2(CH_3)_3SiOH + NH_4Cl$$
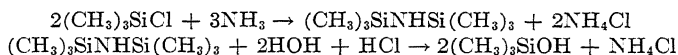
In 1946, Sauer and Hasek (311) reported a survey of the ammonolysis and aminolysis of chlorosilane. Ammonolysis produced hexamethyldisilazine, $(CH_3)_3SiNHSi(CH_3)_3$, the only logical and the only isolable product of the reaction. From all evidence gathered the authors believed that these nitrogen compounds possess a chemistry roughly parallel to that of the hydroxysilanes. They seemed to lose ammonia about as readily as the hydroxy compounds lose water.

Hexamethyldisilazine did not react with metallic sodium but with methylmagnesium iodide as follows:

$$(CH_3)_3SiNHSi(CH_3)_3 + CH_3MgI \rightarrow (CH_3)_3SiN(MgI)Si(CH_3)_3 + CH_4$$
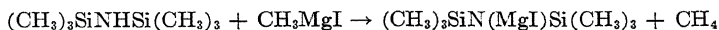
Sauer and Hasek could not make the R_3N compound. This point was considered still another argument in favor of the general concept of the stability and unreactivity of the NH bond in these compounds. There was no reaction with tetrachlorosilane or with trimethylchlorosilane.

Sauer and Hasek found an interesting series of reactions taking place with the amines:

$$(CH_3)_3SiCl + CH_3NH_2 \rightarrow (CH_3)_3SiNHCH_3 + HCl$$
$$(CH_3)_3SiCl + (CH_3)_3SiNHCH_3 \rightarrow (CH_3)_3SiN(CH_3)Si(CH_3)_3 + HCl$$
$$(CH_3)_3SiNHCH_3 + 2HCl \rightarrow (CH_3)_3SiCl + CH_3NH_3Cl$$
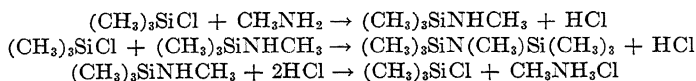
Stock had previously found that hydrochloric acid would cleave hexamethyldisilazine, hence Sauer and Hasek believed that the failure of disilazine to react as did hexamethyldisilazine was due to the previously men-

Table 17.   Synthesis of Silicon Ethers (Classified as to Reactants).

Compound	Reference
1. Na_2SiO_3	590
2. $HSiCl_3$	119, 642
3. H_3SiCl	200, 311
4. $SiCl_4$	1, 38, 42, 60, 83, 116, 118, 119, 128, 129, 162, 200, 222, 283, 293, 294, 295, 296, 300, 302, 304, 305, 306, 307, 308, 310, 317, 322, 323, 355, 376, 409, 443, 444, 497, 511, 512, 513, 514, 545, 554, 583, 586, 587, 591, 641, 646, 655
5. $Cl_3SiSiCl_3$	641
6. $Cl_3SiOSiCl_3$	64, 139, 143, 359, 641, 659
7. $Cl_3SiOSi(Cl)_2OSiCl_3$	143, 659
8. $Cl_3SiO(SiCl_2O)_2SiCl_3$	143
9. $Cl_3SiO(SiCl_2O)_3SiCl_3$	143
10. $Cl_3SiO(SiCl_2O)_3SiCl_3$	143
11. CH_3SiCl_3	119, 132, 583
12. CH_3SiHCl_2	119, 583
13. Cl_3SiSCN	497
14. CH_3SiBr_3	435
15. CH_3COCl	66, 118
16. $C_2H_5SiCl_3$	583
17. $(CH_3)_2SiCl_2$	119, 132, 583, 631
18. $(CH_3)_2SiBr_2$	435
19. $(CH_3)_3SiCl$	119, 309, 311, 583
20. $iC_3H_7SiCl_3$	583
21. $(C_2H_5)_2SiCl_2$	583
22. $tC_4H_9OSiCl_3$	587
23. $Si(SCN)_4$	496, 497
24. $Si(NCO)_4$	497, 510, 512, 659
25. $Zn(C_2H_5)_2$	66
26. $tC_4H_9OSi(OCH_3)Cl_2$	587
27. $tC_4H_9OSi(OC_2H_5)Cl_2$	587
28. $p\text{-}BrC_6H_4SiCl_3$	192
29. $C_6H_5SiCl_3$	51, 83, 408
30. $C_6H_5OSiCl_3$	51
31. $(C_2H_5)_3SiH$	85, 362
32. $(C_2H_5)_3SiCl$	504, 651
33. $(CH_3)_2Si(OC_2H_5)_2$	373, 617, 631
34. $(C_2H_5O)_3SiCl$	305, 554, 556
35. $tC_4H_9OSi(OC_3H_7i)Cl_2$	587
36. $tC_4H_9OSi(OC_4H_9)Cl_2$	587
37. $tC_4H_9OSi(OC_4H_9s)Cl_2$	587
38. $(tC_4H_9O)_2SiCl_2$	587
39. $Si(OC_2H_5)_4$	65, 118, 122, 130, 131, 224, 255, 300, 344, 369, 411, 412, 447, 508, 552, 554, 558, 572, 641, 646, 653

TABLE 17—*Continued*

Compound	Reference
40. $C_2H_5OSi(CH_3)_2OSi(CH_3)_2OC_2H_5$	631
41. $(C_2H_5)_2Si(OC_2H_5)_2$	572
42. $(tC_4H_9O)_2Si(OCH_3)Cl$	587
43. $(iC_3H_7)_3SiCl$	522
44. $(tC_5H_{11}O)_2SiCl_2$	587
45. $(CH_3)_2Si(OC_4H_9s)_2$	631
46. $(tC_4H_9O)_3SiCl$	587
47. $(tC_4H_9O)_2Si(OC_3H_7i)Cl$	587
48. $tC_4H_9OSi(OC_3H_7i)_2Cl$	587
49. $(CH_3)_2Si(OC_4H_9)_2$	132
50. $(C_6H_5)_2SiCl_2$	37, 38, 96
51. $(sC_4H_9O)_3SiCl$	305
52. $(iC_5H_{11}O)_3SiCl$	305, 583
53. $(C_6H_5O)_3SiCl$	51, 83
54. $(C_6H_5)_3SiBr$	324
55. $(C_{12}H_{25}O)_3SiCl$	518
56. $Si(OC_5H_{11}i)_4$	572
57. $(C_{18}H_{37}O)_3SiCl$	518

tioned lethargy of the NH bond. There were also prepared $(CH_3)_3SiNHC_2H_5$, $(CH_3)_3SiN(C_2H_5)_2$ and $(C_2H_5)_3SiNH_2$.

Minnesota Mining and Manufacturing Co. (326) has put on the market compounds of the general formula $ROSi(OR')(NH_2)_2$.

A recent contribution by Miner, Bryan, Holysz and Pedlow (587) has reported quite extensive work on the preparation and properties of molecules with both alkoxyl and amino groups connected to silicon:

$$2tC_4H_9OH + SiCl_4 + 2C_5H_5N \rightarrow 2C_5H_6NCl + (tC_4H_9O)_2SiCl_2$$
$$(tC_4H_9O)_2SiCl_2 + 4NH_3 \rightarrow 2NH_4Cl + (tC_4H_9O)_2Si(NH_2)_2$$
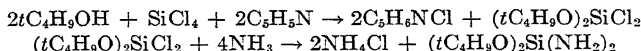
It was possible thus to prepare compounds of the general type $(RO)_x$-$(R'O)_ySi(NH_2)_{4-x-y}$. Reaction of tetrachlorosilane with t-butyl alcohol was complete, and the product generally had been isolated before the second was added. In this manner there were prepared:

$tC_4H_9OSiCl_3$	$tC_4H_9OSi(OCH_3)(NH_2)_2$
$tC_5H_{11}OSiCl_3$	$tC_4H_9OSi(OC_2H_5)(NH_2)_2$
$tC_4H_9OSi(OCH_3)Cl_2$	$tC_4H_9OSi(OC_3H_7i)(NH_2)_2$
$tC_4H_9OSi(OC_2H_5)Cl_2$	$tC_4H_9OSi(OC_4H_9)(NH_2)_2$
$tC_4H_9OSi(OC_3H_7i)Cl_2$	$tC_4H_9OSi(OC_4H_9s)(NH_2)_2$
$tC_4H_9OSi(OC_4H_9)Cl_2$	$(tC_4H_9O)_2Si(NH_2)_2$
$tC_4H_9OSi(OC_4H_9s)Cl_2$	$(tC_5H_{11}O)_2Si(NH_2)_2$
$(tC_4H_9)_2SiCl_2$	$(tC_4H_9O)_3SiNH_2$
$(tC_5H_{11}O)_2SiCl_2$	$(tC_4H_9O)_2Si(OCH_3)NH_2$
$(tC_4H_9O)_3SiCl$	$(tC_4H_9O)_2Si(OC_4H_9)NH_2$
$(tC_5H_{11}O)_3SiCl$	$(tC_4H_9O)_2Si(OC_3H_7i)NH_2$
$(tC_4H_9O)_2Si(OH)_2$	$(iC_3H_7O)_2Si(OC_4H_9t)NH_2$

Physical data for these compounds are listed in Chapter 10.

Table 18.   Reactions of Silicon Ethers with

Substance	Reference
1. H_2	552
2. O_3	572
3. HOH	37, 122, 132, 269, 283, 309, 370, 371, 408, 432, 508, 509, 511, 572, 586, 587, 617, 659
4. Na	51
5. NaOH	427, 515, 617, 641, 642
6. KOH	66, 515
7. NH_3	587
8. PCl_5	124
9. SbF_3	130
10. $SiCl_4$	118, 512, 554
11. HCl	129, 427
12. HBr	51
13. HI	66, 411, 412
14. CH_3OH	1, 510, 558, 580
15. CH_3MgCl	255, 369, 373
16. C_2H_5OH	1, 587
17. LiC_2H_5	449
18. C_2H_5MgCl	255
19. C_2H_5MgBr	255, 305, 361
20. C_2H_5MgI	255
21. $(CH_2OH)_2$	344, 424, 631
22. $CH_2(OH)CH_2NH_2$	302
23. CH_3COCl	1, 51, 66, 118, 504, 572
24. $CH_2(OH)CH(OH)CH_2OH$	344, 424
25. $HCOOC_2H_5$	131
26. $CH_3OCH_2CH_2OH$	641
27. $C_2H_5OCH_2CH_2OH$	641
28. $CH_2(CH_2OH)_2$	631
29. $(CH_2CH_2OH)_2$	631
30. $O(CH_2CH_2OH)_2$	631
31. $Zn(C_2H_5)_2 + Na$	66, 556
32. LiC_3H_7i	522
33. C_4H_9MgCl	255
34. $(CH_3CO)_2O$	118, 355
35. $CH_3COOC_2H_5$	131
36. $CH_2=C(CH_3)COOH$	456
37. $C_5H_{11}MgCl$	255
38. $C_2H_5OCH_2CH(OH)CH_2OH$	300
39. $CO(OC_2H_5)_2$	131
40. $CH_3COOCH_2CH(OH)CH_2OH$	300
41. $CH_3CH(OH)COOC_2H_5$	303
42. $(CH_2CH_2CH_2OH)_2$	127
43. $C_3H_7COOC_2H_5$	131
44. LiC_6H_5	122, 508

TABLE 18—*Continued*

Substance	Reference
45. LiC$_6$H$_4$NH$_2$-p	122, 508
46. LiC$_6$H$_4$CH$_2$OH-p	122, 508
47. C$_6$H$_5$MgBr	305
48. C$_6$H$_5$OH	1
49. LiC$_6$H$_4$CH$_3$-p	122
50. C$_3$H$_7$COOCH$_2$CH(OH)CH$_2$OH	300
51. C$_6$H$_5$COCl	51, 132, 355, 572
52. LiC$_6$H$_3$(CH$_3$)$_2$(2,5)	122, 508
53. C$_6$H$_5$OCH$_2$CH$_2$OH	641
54. LiC$_6$H$_4$N(CH$_3$)$_2$-p	122, 508
55. (CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$OH)$_2$	127
56. C$_{10}$H$_{19}$OH	303
57. C$_3$H$_7$COOCH$_2$CH(OOCC$_3$H$_7$)CH$_2$OH	300
58. LiC$_6$H$_4$C$_6$H$_5$-p	122, 508
59. p-HOC$_6$H$_4$C$_6$H$_4$OH-p	127
60. C$_{17}$H$_{33}$CH$_2$OH	447
61. C$_{17}$H$_{35}$CH$_2$OH	447
62. C$_{17}$H$_{33}$OCOOC$_2$H$_5$	303
63. C$_{17}$H$_{35}$COOCH$_2$CH(OH)CH$_2$OH	300
64. C$_{30}$H$_{61}$OH	303
65. C$_{17}$H$_{35}$COOCH$_2$CH(OOCC$_{17}$H$_{35}$)CH$_2$OH	300

Hydrolysis of di-t-butoxydiaminosilane to di-t-butoxydihydroxysilane was accomplished by ice water, with very little loss of t-butoxyl. The silane diols were not very stable, however. Warm-water hydrolysis formed non-crystalline liquids or resins, but this resinification could be controlled. It was interesting to note that during the resinification of di-t-butoxydiamino-silane there were evolved water, t-butyl alcohol and i-butylene.

Alcoholysis resulted from the action of ethanol. Di-t-butoxydiamino-silane formed di-t-butoxyethoxyaminosilane with evolution of ammonia. The replacement of the second amino group required heat, except when using methanol. The action of secondary alcohols on these amines was slow, especially on the second amino group. The action of tertiary alcohols on even the first of the two amino groups was very slow. Di-t-butoxydichlorosilane with ethanol and pyridine gave di-t-butoxydiethoxy-silane.

It was also found that primary amino groups could be displaced by amines with release of ammonia, and that organic acids reacting on these diamino compounds gave rise to esters:

$$(tC_4H_9O)_2Si(NH_2)_2 + 2RNH_2 \rightarrow (tC_4H_9O)_2Si(NHR)_2 + 2NH_3$$
$$(tC_4H_9O)_2Si(NH_2)_2 + 4RCOOH \rightarrow (tC_4H_9O)_2Si(OOCR)_2 + 2RCOONH_4$$
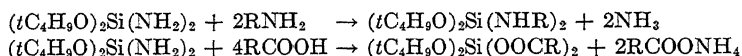
When *t*-butoxytrichlorosilane was treated with ammonia a polymer resulted which evolved ammonia slowly over a considerable period of time.   When heated at 200°, di-*t*-butoxydiaminosilane also evolved ammonia:

$$x(t\text{C}_4\text{H}_9\text{O})_2\text{Si}(\text{NH}_2)_2 \text{ (in weak acid)}(200°) \rightarrow x\text{NH}_3 + [(t\text{C}_4\text{H}_9\text{O})_2\text{SiNH}]_x$$
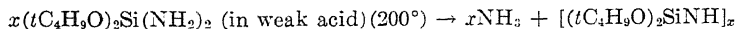
Under the heading of possible applications of these compounds, the authors listed them as water-repellent mixtures on any solid surface and as antistripping agents for "road aggregates."

From this work it may be said, in the words of the authors, that tertiary alkoxyl groups are more resistant to hydrolysis than others, that the stability of the substituted silanes is increased as the number of these tertiary groups is increased, and that in general they are more stable in alkalies than in acids.

Sommer presented modifications of the reaction between sulfuric acid and hexamethyldisiloxane.   Further, in heptane solution, di-trimethylsilicyl sulfate reacted with gaseous sulfuric acid.   Ammonia (652) reacts with di-trimethylsilicyl sulfate forming ammonium sulfate and di-trimethylsilicyl amine.

Bailey, Sommer and Whitmore (651) treated triethylchlorosilane with ammonia obtaining triethylaminosilane and ammonium chloride.   Similarly, diethyl-α-chloroethylchlorosilane formed diethyl-α-chloroethylaminosilane.   The amino group could be converted to halogen by the action of (1) HCl, gas, (2) HBr, (3) HCl (concentrated solution), (4) HF (concentrated solution) and (5) HBr in H_2SO_4.   Physical constants were presented for the following compounds, triethylaminosilane, diethyl-α-chloroethylaminosilane,   triethylchlorosilane,   diethyl-α-chloroethylchlorosilane, triethylfluorosilane, diethyl-α-chloroethylfluorosilane, triethylbromosilane and diethyl-α-chloroethylbromosilane.

Chapter 9

Nomenclature

To many the introduction to a new branch of science is like learning a new language. To no one is this more true than to the worker in the field of silico-organic chemistry. This science is so new that a complete set of logical names and roots can be set up without hindrance by any of the inhibitions which attach to large sections of carbon organic chemistry, arising from long continued usage of popular names.

Thus Kipping (2) first formally suggested "silicane" for SiH_4. Later (16) he listed "silicyl" for SiH_3, leading to such words as "triphenylsilicyl chloride" for $(C_6H_5)_3SiCl$. Others suggested here were

silicanol for H_3SiOH
silicanediol for $H_2Si(OH)_2$
diethylsilicone for $(C_2H_5)_2SiO$

Kipping preferred not to use the word "ether" for the last compound because of the difference in chemical properties between the silicon compound and carbon ethers. There followed:

anhydrobisdiphenylsilicanediol

$$\underset{HO}{\overset{C_6H_5}{\diagdown}}\!C_6H_5\!-\!Si\!-\!O\!-\!Si\!-\!C_6H_5\!\underset{OH}{\overset{C_6H_5}{\diagup}}$$

dianhydrotrisdiphenylsilicanediol

$$C_6H_5\!-\!Si\!-\!O\!-\!Si\!-\!O\!-\!Si\!-\!C_6H_5$$

trianhydrotrisdiphenylsilicanediol

$$(C_2H_5)_2Si \quad Si(C_6H_5)_2$$
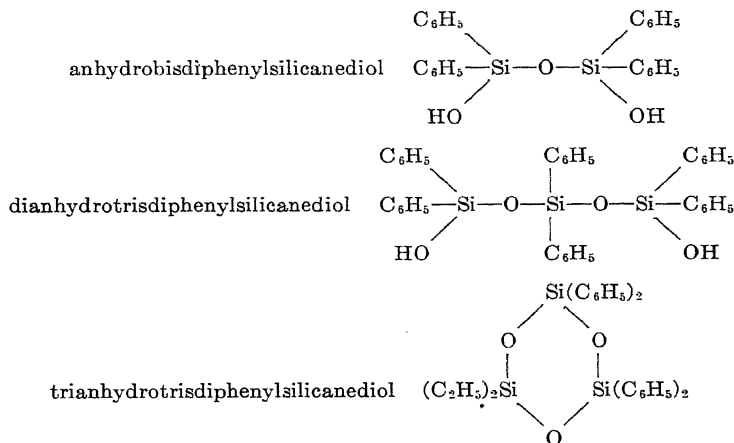
Alfred Stock (150) laid the foundations for his own system of silico organic nomenclature. He favored "silane," "disilane," "trisilane," etc., for

SiH_4, Si_2H_6, Si_3H_8. These names would then lead to "silene" for Si_2H_4 and "disilene" for Si_4H_8. H_3Si would be "monosilyl" or perhaps "monosilanyl," and Si_2H_5 would be "disilyl." $HSiCl_3$ was termed "trichloromonosilane."

Stock listed several terms proposed in the past by others, without giving them too much approval, including Ladenburg's "silicols" (66) and his "siliconic acid" (67) as well as Kipping's "silicane," "silicyl" and "silicanol." Ladenburg's siliconic acid will have to give way, said Stock, to something more scientific when silico organic chemistry becomes more complicated.

Stock suggested "silicopropane" for $C_2H_5SiH_3$ and "persilicopropane" for Si_3H_8, but apparently "ethylsilane" was preferred for the former.

As a final comment, Stock mentioned the distinction made by Friedel and Ladenburg (292) between "silicopropionic ester,' $C_2H_5Si(OC_2H_5)_3$ and "silicon propionic ester" $Si_3H_5(OC_2H_5)_3$. Stock felt that the distinction was too fine and could only lead to error.

As a corollary to reference 150, Stock presented (148) in the following year, an interesting and critical comparative survey of silicon and carbon organic chemistries, including a few further observations on the subject of nomenclature. In the same year his third paper of this series (146) dealt more exclusively with nomenclature. Stock suggested

<div align="center">

disiloxane for $H_3SiOSiH_3$

</div>

<div align="center">

prosiloxane for H_2SiO

</div>
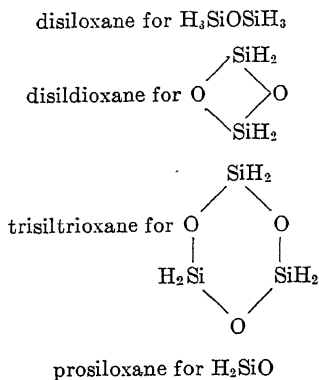
In connection with these compounds (except the first) Stock considered them not as anhydrides, as did Kipping (16), but as polymerized "prosiloxane." Continuing, there appeared "oxyprosiloxane', $HSiOOH$.

Stock closed this paper with a few truly original observations. The similarity between silicon and carbon chemistries, he concluded, is merely superficial. Therefore investigators should shut out all memories of the nomenclature of carbon compounds, especially those based on poor foundations, and strike out in new and more logical directions. Especially he recommended use of "oxo" and "oxy" in describing substituted silanes.

The American Chemical Society has given serious study to the matter of the nomenclature of organic compounds of silicon. As a result there appeared, in 1944, a contribution by Dr. Robert O. Sauer (288) which is reproduced herewith because of its exceptional value.

"An organosilicon compound is a compound containing at least one carbonsilicon bond. The first molecule of this type (except, of course, silicon carbide) was reported in 1863 and the number of organosilicon compounds of known structure has increased steadily, particularly since about 1900. More recently this class of substances has begun to assume industrial importance. In view of (*a*) the present greatly increased interest in this field, (*b*) the possibility of existence of numerous and complex organosilicon molecules, and (*c*) the indefinite state of their nomenclature at the present time, it seems appropriate to discuss the development of the several schemes of nomenclature now in use and to recommend some unifying generalizations. These recommendations are the result of several years' actual contact with the problem of organosilicon nomenclature and represent, it is believed, a considerable improvement in precision and . euphony over existing terminology.

Kipping was the first to feel the necessity for a scheme of nomenclature which could be rationally expanded to name compounds as yet unknown to him. He chose the root *silicane* for the simplest silicon hydride, SiH_4, and its derivatives. From this root the following compounds and group were named: H_3SiOH, silicanol; $H_2Si(OH)_2$, silicanediol; H_3Si-, silicyl. For the higher silicon hydrides, *e.g.*, Si_2H_6, Si_3H_8, etc., Kipping appears by his usage to prefer the names: silicoethane, silicopropane, etc., although he makes no definite statement on the subject. In spite of the fact that he proposed the name silicanol for the compound H_3SiOH and its derivatives, he consistently used the term silicol, which term appears to have originated with Ladenburg.

The intermolecular dehydration product of a silicol (silicanol) was termed by Kipping a silicyl oxide, *e.g.*, $(C_6H_5)_3SiOSi(C_6H_5)_3$, triphenylsilicyl oxide. The hypothetical monomers derived by intramolecular dehydration of the silicanediols were termed silicones; thus, $(C_2H_5)_2SiO$ was diethylsilicone. The products formed by intermolecular dehydration of a silicanediol were named as derivatives of the parent diol by indicating in the name the number of molecules of water removed and the number of silicanediol molecules condensing to form the new compound. Thus, $[(C_6H_5)_2SiO]_3$, a polysilicone, was referred to as trianhydrotrisdiphenylsilicanediol and $HOSi(C_6H_5)_2OSi(C_6H_5)_2OH$ as anhydrobisdiphenylsilicanediol.

In the preceding paragraph we have noted that Kipping referred to compounds of the empirical formula R_2SiO ($R =$ an organic radical or hydrogen) as silicones or polysilicones. This usage seems to have been based on

a formal analogy with ketones in carbon chemistry; however, the analogy is an unfortunate one because compounds of the formula R_2SiO have been isolated in only polymeric forms. Wöhler appears to use the term silicone to designate a compound of hydrogen, silicon, and oxygen (of unknown structure, but presumably containing silicon-silicon, silicon-oxygen and silicon-hydrogen bonds). In this laboratory the term polysilicone or, simply, *silicone* is used to designate high molecular weight products of the empirical formula $R_NSiO_{(4-n)/2}$ where N, the R/Si ratio, is less than three. In general, the exact structure of these polymers is unknown. It is emphasized that this usage—which conflicts with both the Kipping definition and Wöhler's usage (and these conflict with each other)—is really an expedient extension of the Kipping terminology in order to classify a wide variety of organosilicon polymers and is not applicable to compounds of precisely known structure.

Shortly after Kipping's proposal, Martin suggested the root names: "silicose" for compounds containing silicon-silicon bonds, and "silicate" for compounds containing the silicon-oxygen-silicon linkage. These names were intended for organic as well as for inorganic compounds of silicon, but the proposal failed to become popular.

Stock, who was active in the field of silicon hydrides, proposed the somewhat shorter root of *silane* (pronounced sī'-lāne) for these compounds, prefixing this root in order to designate the number of silicon atoms in the chain. Thus, SiH_4 was monosilane, H_3Si—SiH_3 was disilane, and H_3Si—SiH_2—SiH_3 was trisilane. However, Stock did not rule out entirely the older scheme by which alkyl silicon hydrides were named as silicohydrocarbons, apparently believing that it was sometimes of value to preserve the analogy with familiar hydrocarbons. If all the carbon atoms of a hydrocarbon structure were replaced by silicon, this compound might then be designated according to Stock as a "persilico" hydrocarbon. For example, CH_3SiH_3 could be named silicoethane as well as methylsilane, and Si_3H_8 could be persilicopropane as well as trisilane.

Stock was also interested in the oxygenated derivatives of the silanes. The unstable monosilanol, H_3SiOH, dehydrated yielding $H_3SiOSiH_3$, which Stock termed *disiloxane*, that is to say, two silicon atoms joined by one oxygen. Other compounds of this class which Stock named $(H_2SiO)_2$, disildioxane (two silicon and two oxygen atoms); and $[(C_6H_5)_2SiO]_4$, octaphenyltetrasiltetraoxane. The monomeric R_2SiO from which these latter two may be considered to have been derived were designated as oxomonosilanes, the parent compound H_2SiO, however, being termed "prosiloxane". At this time, Stock sought to discourage naming silicon compounds according to the carbon analogs and to replace monosilanol with oxy-monosilane, monosilanediol with dioxy-monosilane and monosilanone with oxo-monosilane.

In choosing a system of nomenclature or in devising a new one, especial emphasis should be placed on clarity, brevity, uniformity, and euphony if the system is to attain general acceptance. Our first decision concerns the selection of the nomenclature root for the organosilicon compounds, this involving a choice between the terms silicane and silane. The latter is a shorter term and more adaptable to euphonious derivations than silicane although Kipping's root may perhaps enable more rapid recognition of the relation to the element silicon. As used by Kipping, silicane was not applied to compounds having silicon-silicon bonds, although this does not preclude our using the term disilicane for derivatives of Si_2H_6.

The principal difficulty with the silicane root for everyday use is the length (an extra syllable) and consequent lack of euphony in the names of the derivatives. Kipping must have realized this, for although his proposed name for compounds of the type R_3SiOH (R = an organic radical or hydrogen) was silicanol he used the term silicol in his publications. The more pleasing character of the silane root is easily demonstrated by repeating aloud the names of a few derivatives using both systems, *e.g.*, diphenylsilanediol, diphenylsilicanediol; silyl, silicyl; silanol, silicanol (or silicol).

Another distinctive advantage to the scheme based on the silane root is its ready extension to compounds containing numerous silicon-oxygen-silicon (siloxane) linkages; this extension is overly clumsy using the silicane root. All in all, it seems as though *silane* should be the more widely used of the two roots; this is the one we have chosen. It should prove advantageous to omit Stock's prefix (mono) to this root for derivatives of SiH_4. Thus, $(C_2H_5)_2SiCl_2$ becomes diethyldichlorosilane, but $(CH_3)_3Si—Si(CH_3)_3$ is hexamethyldisilane.

The decision concerning the root having been made, the hydroxy silicon compounds are best named as -ols according to the Kipping system. Thus, $(C_2H_5)_3SiOH$ is triethylsilanol and $(C_6H_5)_2Si(OH)_2$ is diphenylsilanediol.

The dehydration products of the silanols, variously referred to as siloxanes (pronounced sĭ′-lŏx-āne), silicyl oxides, or silyl ethers, are most advantageously named as *siloxane* derivatives. Since Stock assigned the term disiloxane to $H_3SiOSiH_3$, we shall refer to $(C_2H_5)_3SiOSi(C_2H_5)_3$ as hexaethyldisiloxane.

This terminology is readily extended to compounds containing several siloxane linkages. For example, in naming silicon oxychlorides of the formula $Cl_3Si[OSiCl_2]_nCl$ (where $n = 1, 2, 3 \ldots$) we shall designate the number of silicon atoms in the siloxane chain, that is, $n + 1$, simply by the proper prefix to siloxane (omitting Stock's prefix to the -oxane ending). Thus, the compound $Cl_3SiOSiCl_2OSiCl_3$ is called octachlorotrisiloxane. If the substituents on such a polysiloxane are not all of the same kind their number and position may be indicated by numbering the atoms of the chain

and by using these numbers in conjunction with the appropriate prefix and/ or suffix to the polysiloxane root. For example, $HOSi(C_6H_5)_2OSi(C_6H_5)_2OH$ becomes tetraphenyldisiloxane-1,3-diol. Cyclic condensation products of the silanediols can be satisfactorily described by merely prefixing cyclo to the same name one would assign if the molecule were linear. According to this system $[(C_6H_5)_2SiO]_3$—which Kipping called trianhydrotrisdiphenyl-silicanediol—becomes hexaphenylcyclotrisiloxane.

In naming compounds having branched siloxane chains, or siloxane rings with siloxane side chains, it should prove satisfactory to use the term siloxy- for the group R_3SiO—. The radicals R_3Si— and R_3Si— SiR_2— may be termed silyl and disilanyl, respectively. The name for the latter was suggested by Dr. Austin M. Patterson, to whom this paper went for review, in order to distinguish the latter radical from two R_3Si—groups.

By analogy with the siloxanes, compounds of the general formula R_3Si $(NR—SiR_2)_nR$—where R has the same significance as before—are designated as *silazines*. Thus, according to this suggestion $(C_2H_5)_3Si$—NH— $Si(C_2H_5)_3$ becomes hexaethyldisilazine, and CH_3N=$(SiH_3)_2$ becomes 2-(or N-) methyldisilazine. It seems preferable to designate compounds of the type R_3SiNR_2' as silylamines, *e.g.*, $H_3SiNHCH_3$, N-silylmethylamine.

At present, the nomenclature of the alkyl ethers (or esters) of the silanols, silanediols, and silanetriols appears quite inconsistent within the group. Compounds of the general formulas R_3SiOR' and $R_2Si(OR')_2$ have been referred to as trialkyl (or aryl) monosilanol alkyl ethers and dialkyl(or aryl) monosilanol dialkyl ethers, respectively. Compounds of the general formula $RSi(OR')_3$, however, have been termed trialkyl hydrocarbon-orthosiliconates, *e.g.*, triethyl methaneorthosiliconate for $CH_3Si(OC_2H_5)_3$, or named as ortho esters of silico organic acids, *e.g.*, ethyl orthosilicoacetate for $CH_3Si(OC_2H_5)_3$. One also sometimes sees a reference to esters of alkyl monosilane acids.

The foregoing terms, though descriptive, are not self-consistent. They also appear somewhat artificial since the silanetriols (acids?) in the case of the last example are unknown. It would seem more appropriate to include compounds of the general type $R_nSi(OR')_{4-n}$, (where R and R' are organic radicals and n may have the values 1, 2, or 3) in the generic term silane and avoid inconsistency by naming the compounds mono-, di-, or trialkoxy (or aryloxy) silanes.

In summary, the purpose of this paper has been to discuss briefly the present situation of nomenclature in the organosilicon field and to select a scheme deemed reasonably precise and internally consistent. This system has been based on the following five generalizations.

1. Organosilicon compounds of the general formula $R[SiR_2]_nSiR_3$ where R may be an organic radical, hydrogen, halogen, an alkoxy or an aryloxy group and $n = 0, 1, 2, \ldots$ are named as *silane* derivatives.

2. Organosilicon compounds containing Si—O—Si linkages are named as *siloxane* derivatives.

3. Organosilicon ring compounds of the general formula $[R_2SiO]_n$ where R has the same significance as in *1* and $n = 2, 3, 4, \ldots$ are named as *cyclo-siloxanes*.

4. In organosilicon compounds containing one or more hydroxyl groups attached to silicon the name is formed by adding the suffixes *-ol, -diol, -triol*, etc. (corresponding to the number of hydroxyl groups per molecule) to the proper root name (*see 1, 2,* and *3*).

5. Organosilicon compounds of the type formula $R[SiR_2NH]_nSiR_3$ where R has the same significance as in *1* and $n = 1, 2, 3, \ldots$ are named as *silazine* derivatives.

Table 1 lists a few of the simple known compounds representative of the types under discussion. Names have been assigned using the current systems of nomenclature, and these names are to be compared with those suggested in the last column.

Acknowledgment. The author gratefully acknowledges the helpful criticism of the several members of the General Electric research staff who have had occasion to use this system and is particularly indebted to Drs. W. I. Patnode, E. G. Rochow, and M. M. Sprung for valuable suggestions during the evolution of the views presented here."

Patterson (551) and associates have written a guide to the searcher for silicon compounds in the indices of *Chemical Abstracts*.

Of no less value has been a section of the report of the current American Chemical Society committee covering nomenclature. This report (289) also is reproduced below, as the last word in attempts at harmonization and co-ordination along these lines.

"Interest in chemical nomenclature is at a high peak. There is much evidence of this. Your committee has been endeavoring to serve as a sort of clearing-house for information as to suitable names for compounds, and the number of inquiries has become increasingly large. Requests for nomenclature pamphlets were never so numerous. Over 4,000 orders for copies of the Definitive Report have been filled. Other available pamphlets, listed below, are in strong demand.

A Committee on Nomenclature recently organized by the Organic Division is going enthusiastically to work. It has been the policy of your committee for several years to encourage the organization of committees within the divisions of the SOCIETY, for there is much more to be done than any single group of chemists, already busy with other things, can do as spare-time work, and, furthermore, the special knowledge, the interest, and the enthusiasm of specialists are needed for problems in specific fields. Your committee endeavors to help to bring decisions by such groups into harmony

Comparison of the Several Nomenclature Systems.

Compound Formula	Kipping's System	Stock's System	Other Usage	Suggested Names
$(CH_3)_3SiC_2H_5$	Trimethylethylsilicane	Trimethylethylmonosilane	Trimethylethyl silicon	Trimethylethylsilane
$(CH_3)_2SiCl_2$	Dimethyldichlorosilicane	Dimethyldichloromonosilane	Dimethyl silicon dichloride	Dimethyldichlorosilane
$(CH_3)_3Si—Si(CH_3)_3$	Hexamethylsilicoethane	Hexamethyldisilane		Hexamethyldisilane
$(C_2H_5)_3SiOH$	Triethylsilicanol	Triethylmonosilanol	Triethylsilicol	Triethylsilanol
$(C_6H_5)_2Si(OH)_2$	Diphenylsilicanediol	Diphenylmonosilanediol	...	Diphenylsilanediol
$(C_2H_5)_3SiOSi(C_2H_5)_3$	Triethylsilicyl oxide	Hexaethyldisiloxane	Triethylsilyl ether	Hexaethyldisiloxane
$Cl_3SiOSiCl_2OSiCl_3$	?	Octachlorotrisildioxane	..	Octachlorotrisiloxane
$HO(C_6H_5)_2SiOSi(C_6H_5)_2OH$	Monoanhydrobisdiphenylsilicanediol	?		Tetraphenyldisiloxane-1,3-diol
$[(C_6H_5)_2SiO]_3$	Trianhydrotrisdiphenylsilicanediol	Hexaphenyltrisiltrioxane	Cyclic diphenyltrisiloxane	Hexaphenylcyclotrisiloxane
$(C_2H_5)_3SiNHSi(C_2H_5)_3$	...	Di(triethylmonosilyl)amine	Di(triethylsilicyl)amine	Hexaethyldisilazine
$(C_2H_5)_3SiOC_2H_5$	Triethylethoxysilicane(?)	Triethylethoxymonosilane	Triethylsilicol ethyl ether	Triethylethoxysilane
$(C_6H_5)_2Si(OC_2H_5)_2$	Diphenyldiethoxysilicane(?)	Diphenyldiethoxymonosilane	Diphenylsilicol diethyl ether	Diphenyldiethoxysilane
$C_6H_5Si(OC_2H_5)_3$	?	Phenyltriethoxymonosilane	Triethyl benzeneorthosiliconate; ethyl orthosilicobenzoate	Phenyltriethoxysilane

with general nomenclature considerations, to make them fit into the whole picture as outlined by accepted nomenclature rules.

One reason for increased interest in chemical nomenclature is the growing need for means of recording information concerning chemical compounds. Compounds were studied in large numbers, for example, in connection with a number of wartime problems. These problems have emphasized the need for keeping chemical nomenclature systematic.

With the very helpful cooperation of a number of chemists interested in organosilicon compounds (H. S. Nutting, Robert O. Sauer, A. J. Barry, W. H. Daudt, M. J. Hunter, and Murray Sprung met in conference with four members of the ACS committee, while others helped by correspondence), the rules on the naming of silicon compounds given below were worked out. These rules have been adopted by your committee of twenty-three (unanimously, except that one member has reserved his vote on rule 17). A note published in *Chemical and Engineering News* invited partipation in this work and all who responded were given such an opportunity. Much preliminary work was done by the gentlemen above mentioned, with the additional help of C. L. Moyle and E. L. Warrick.

Nomenclature of Silicon Compounds

The recommendations which follow worked out to help in naming organosilicon compounds (compounds containing at least one carbon-silicon bond), are not intended to rule out the use of established inorganic names, as silicon tetrachloride for $SiCl_4$.

1. The combining form *sil-*, rather than silic-, will be used in forming the names of organosilicon compounds and radicals.

2. The name of the compound SiH_4 will be *silane*. Compounds having the general formula $H_3Si(SiH_2)_nSiH_3$ will be called *disilane, trisilane*, etc., according to the number of silicon atoms present. Compounds of the general formula $Si_nH_{2n} + 2$ will have the generic name *silanes*. They will be named according to the longest chain present.

3. Compounds having the formula $H_3Si(OSiH_2)_nOSiH_3$ will be called *disiloxane, trisiloxane*, etc., according to the number of silicon atoms present; they will have the generic name *siloxanes*.

4. Compounds having the formula $H_3Si(NHSiH_2)_nNHSiH_3$ will be called *disilazane, trisilazane*, etc., according to the number of silicon atoms present; they will have the generic name *silazanes*.

5. Cyclic silicon compounds having the formula $(SiH_2)_n$ will be called *cyclotrisilane, cyclotetrasilane*, etc., according to the number of members in the ring; they will have the generic name *cyclosilanes*.

6. Cyclic compounds having the formula $(SiH_2 \cdot O)_n$ will be called *cyclodisiloxane, cyclotrisiloxane*, etc., according to the number of silicon atoms in the ring. They will have the generic name *cyclosiloxanes*.

7. Cyclic compounds having the formula $(SiH_2 \cdot NH)_n$ will have the generic name *cyclosilazanes* and will be named similarly to the cyclosiloxanes. Example:

$\overline{NH \cdot SiH_2 \cdot NH \cdot SiH_2}$, cyclodisilazane.

8. Polycyclic siloxanes (including spiro compounds) will be named by The Ring Index method adapted, as shown by the examples, to the use of the root siloxane, which is preceded by a prefix indicating the number of silicon atoms in the ring system. The system of numbering will follow that used in The Ring Index.
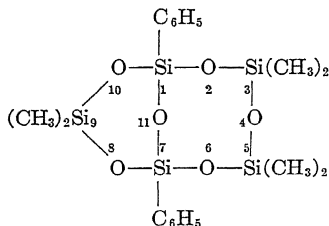
3,3,5,5,9,9-Hexamethyl-1,7-diphenylbicyclo[5.3.1]-pentasiloxane
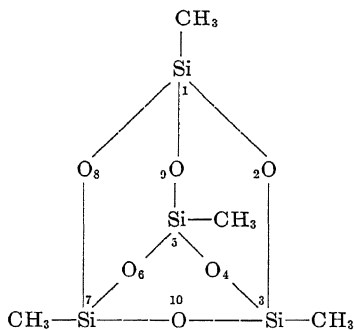
Tetramethyltricyclo[3.3.1.1^{3,7}]-tetrasiloxane
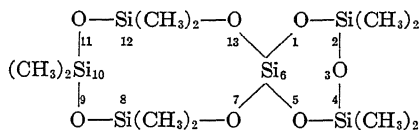
Decamethylspiro[5.7]hexasiloxane

9. With the exception of the cyclosiloxanes, the cyclosilazanes, and the polycyclic siloxanes, which shall be named by rules 6, 7, and 8, respectively, heterocyclic ring systems containing Si will be named according to The Ring Index rules.

10. The following list of names of radicals containing silicon is adopted; it illustrates the principles on which any further radical names should be formed. Compound radical names may also be formed in the usual manner; as, $(C_6H_5)_3Si—$, triphenylsilyl; $(H_3Si)_3Si—$, 1,1-disilyldisilanyl.

$H_3Si—$	silyl
$H_2Si<$	silylene
$HSi\equiv$	silylidyne
$H_3SiSiH_2—$	disilanyl
$—SiH_2SiH_2—$	disilanylene
$H_3SiSiH_2SiH_2—$	trisilanyl
$(H_3Si)_2SiH—$	1-silyldisilanyl

$$—SiH_2SiH_2SiH_2— \qquad \text{trisilanylene}$$
$$H_3SiOSiH_2— \qquad \text{disiloxanyl}$$
$$H_3SiNHSiH_2— \qquad \text{disilazanyl}$$
$$H_3SiO— \qquad \text{siloxy}$$
$$H_3SiNH— \qquad \text{silylamino}$$
$$H_3SiSiH_2O— \qquad \text{disilanoxy}$$
$$H_3SiSiH_2NH— \qquad \text{disilanylamino}$$
$$H_3SiOSiH_2O— \qquad \text{disiloxanoxy}$$
$$H_3SiOSiH_2NH— \qquad \text{disiloxanylamino}$$
$$H_3SiNHSiH_2O— \qquad \text{disilazanoxy}$$
$$H_3SiNHSiH_2NH— \qquad \text{disilazanylamino}$$

11. Hydroxy derivatives in which OH is attached to silicon will be named by adding the suffixes *ol*, *diol*, *triol*, etc., to the name of the parent. Examples: H_3SiOH, silanol; $H_3Si(OH)_2$, silanediol; $HSi(OH)_3$, silanetriol; $Si(OH)_3Si(OH)$ disilanehexol;

$$\begin{array}{ccccc} HO & OH & CH_3OH & & \\ | & \diagdown\diagup & | & & \\ (CH_3)_2Si—O—Si—O—Si(CH_3)_2, \\ 5 & 4 & 3 & 2 & 1 \end{array}$$
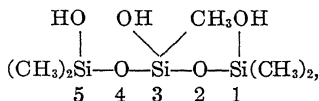
1,1,3,5,5-pentamethyltrisiloxane-1,3,5-triol. In certain cases the OH group may be expressed by the prefix hydroxy as in

$$\begin{array}{c} HOH_2SiSiH_2SiH_2OH \\ 4\ 3 \qquad | \\ SiHSiH_2OH, \\ 2 \quad 1 \end{array}$$
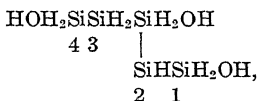
2-(hydroxysilyl)tretrasilane-1,4-diol.

12. Other substituents, both functional atoms or groups and hydrocarbon radicals attached to silicon will be expressed by appropriate prefixes. Examples: $H_2Si(OC_2H_5)_2$, diethoxysilane; $H_2Si:O$, oxosilane; $H_2Si:NH$, iminosilane; $HSi(:O)OH$, oxosilanol; $Cl_3SiOSiCl_3$, hexachlorodisiloxane; $(n\text{-}C_4H_9)_2SiCl_2$, dibutyldichlorosilane.

13. For designating the positions of substituents on a straight open chain containing silicon atoms with or without other members, each member of the chain will be numbered, from one terminal silicon atom to the other; end groups not containing silicon will be regarded as substituents. Silicon-containing ring systems will be numbered according to accepted practice. Examples:

$$\begin{array}{ccc} H_3SiSiH_2SiH_3; & H_3Si\cdot O\cdot SiH_2OH; & \overline{O\cdot SiH_2\cdot SiH_2\cdot SiH_2.} \\ 1\ 2\quad 3 & 3\quad 2\ 1 & 1\quad 2\quad 3\quad 4 \end{array}$$
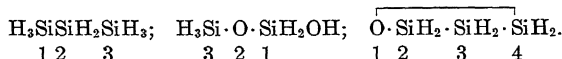
When two or more possibilities for numbering occur, the same principles will be followed as for carbon compounds.

14. Compounds in which metals are combined directly with silicon are, in general, named as derivatives of the metal; as, $(C_6H_5)_3SiLi$, (triphenylsilyl)-lithium. However, in exceptional cases, the metal may be named as a substituent; as, sodium *p*-sodiosilylbenzoate

$$NaOOC\hexagon SiH_2Na.$$

15. The question of special class names for derivatives in series characterized by a regularly recurring unit, and in general the naming of high-molecular products in terms of their units, is reserved for further discussion.

While all of the rules are open to revision if possibility for improvement becomes apparent, the committee feels that it should emphasize the tentative nature of rules 16, 17, 18, and 19, which follow, and with reference to them in particular, should invite comment, whether it be in objection or in the form of a "vote" for their retention.

16. Metallic salts of hydroxy derivatives may be named by changing *ol* to *olate* and placing the name of the metal before; as, $(C_6H_5)_3SiONa$, sodium triphenylsilanolate. The form "sodium salt of triphenylsilanol" or "triphenylsilanol, sodium salt" may also be employed.

17. The order in which prefixes are stated in a name will be the alphabetic one.

18. Compounds containing carbon as well as silicon are named as silicon derivatives except in those cases where there are reactive groups—e.g., NH_2, OH—in the organic portion and none directly attached to silicon. Exceptions are permitted where this rule leads to cumbersome names. Examples:

$H_3SiOC_2H_5$	ethoxysilane
$H_2Si(OC_2H_5)_2$	diethoxysilane
$(CH_3)_3SiSCH_3$	trimethyl(methylmercapto)silane
$H_3SiNHCH_3$	methylaminosilane
$HSi(NHCH_3)_3$	tris(methylamino)silane
H_3SiCH_2Cl	(chloromethyl)silane
$R_3SiOOCCH_3$	trialkylsilanol acetate or acetoxytrialkylsilane
$R_2Si(OOCCH_3)_2$	dialkylsilanediol diacetate or diacetoxydialkylsilane
$(CH_3)_3SiCH_2CONHC_6H_5$	α-(trimethylsilyl)acetanilide
$Cl_3SiCH(OH)CH_3$	trichloro(1-hydroxyethyl)silane
$R_2Si(OH)CH(OH)CH_3$	dialkyl(1-hydroxyethyl)silanol
$R_3SiCH_2CH_2OH$	2-(trialkylsilyl)ethanol

19. Since the term *silicone* has acquired an industrial meaning and is no longer approved as a name for $H_2Si:O$, it would seem that the industrial chemists dealing with "silicones" are the ones to agree on its meaning. This should perhaps be determined by actual usage rather than theoretical considerations.

Pronunciation. Pronunciation experts and dictionaries are influenced a good deal by usage, but other considerations, such as clarity and phonetic patterns, are given due consideration in dealing with new words. They consider it better in general for names such as those discussed in the above rules to follow the pronunciation of the primitive word as closely as possible. Since the "i" in a silicon is short the tendency would be in the direction of the use of a short "i" for the derived names of silicon compounds. This appears to be happening for names in which the combining form "sil" is followed by "i" or a consonant, as in silicate, silicone, and silthiane. Apparently, however, when "sil" is followed by a vowel other than "i" those working with these compounds are tending to use the long "i" as in silane and siloxane. Usage seems likely to be the determining factor and this report records these tendencies in the belief that they will continue and to encourage uniformity.

Publications on Nomenclature

Five members of your committee cooperated in the production of the 109-page Introduction to the 1945 Subject Index to *Chemical Abstracts*, which is devoted almost exclusively to the naming of chemical compounds for indexing. This is mentioned here not as official committee work, but because it is thought to be of interest as an example of the application of ACS committee rulings and of those of the International Union of Chemistry in a comprehensive manner, with many examples, in systematic naming for a special purpose, indexing. Reprints of this nomenclature discussion are now available at 50 cents from the office of the committee chairman, along with the following other nomenclature pamphlets:

(*a*) Definitive Report of the Commission on the Reform of the Nomenclature of Organic Chemistry. Translation with comments and index by Austin M. Patterson. Price 10 cents.

(*b*) Rules for Naming Inorganic Compounds. Report of the Committee of the International Union of Chemistry for the Reform of Inorganic Chemical Nomenclature, 1940. Price 10 cents. The committee has provided an American version of the Rules.

(*c*) The Pronunciation of Chemical Words. A committee report. Price 5 cents.

(*d*) Nomenclature of the Hydrogen Isotopes and Their Compounds. A committee report. No charge.

(*e*) Directions for Assistant Editors and Abstractors of *Chemical Abstracts*. Price 10 cents. Much concentrated information on chemical nomenclature, symbols, forms and abbreviations is assembled in this 29-page booklet in form convenient for use.

(*f*) The Standardization of Chemical Nomenclature. No charge. This reprint of an article by the committee chairman contains a list of references to sources of information on chemical literature.

C. L. Comar, D. L. Fox, Gordon Mackinney, Paul Rothemund, Harry H. Sobotka, L. Zechmeister, F. P. Zscheile, and, in particular, Harold Strain cooperated with J. Murray Luck, chairman of the Committee on Biochemical Nomenclature of the National Research Council, in preparing a report on the nomenclature of carotenoid pigments. The various drafts of the report prepared during the course of this study were the work of Dr. Strain, who, along with H. A. Mattill, is a member of Dr. Luck's committee. A member of the ACS committee, Austin M. Patterson, helped in this work also and your committee as a whole was given the privilege of reviewing the report. It was readily and unanimously endorsed and is included as an appendix in this report, as a means of recommending it officially to ACS members.

E. J. CRANE, *Chairman*"

Chapter 10

Physical Properties

HSiFCl$_2$	Fluorodichlorosilane: m.p. $-149.5°$, b.p. $-18.4°$ (760 mm) (233).
HSiF$_2$Cl	Difluorochlorosilane: m.p. $-50°$ (233).
HSiCl$_3$	Trichlorosilane: b.p. 31.8° (760 mm), m.p. $-128.2°$ (232).
HSiBr$_3$	Tribromosilane: b.p. 115°–117° (760 mm) (165).
H$_2$SiF$_2$	Difluorosilane: b.p. $-77.5°$ (760 mm), m.p. $-119.1°$ (217).
H$_2$SiCl$_2$	Dichlorosilane: m.p. $-112°$, b.p. 8° (760 mm), d $(-122°)$ = 1.42 (98).
H$_2$SiBr$_2$	Dibromosilane: m.p. 70.1°, b.p. 18° (123 mm), d (0°) = 2.14 (144).
H$_2$SiI$_2$	Diiodosilane: b.p. 45.8° (760 mm), m.p. $-56.5°$ (217).
H$_3$SiF	Fluorosilane: b.p. $-97.5°$ (760 mm), m.p. $-131.2°$ (233).
H$_3$SiCl	Chlorosilane: b.p. $-30.5°$ (760 mm), m.p. $-118°$, d $(-113°)$ = 1.145 (98).
H$_3$SiBr	Bromosilane: m.p. $-94°$, b.p. $-1.0°$ (760 mm), d (0°) = 1.535 (144).
H$_3$SiI	Iodosilane: b.p. 45.4° (760 mm), m.p. $-57°$, d (0.5°) = 2.0700, d (14.8°) = 1.20350 (227).
H$_4$Si	Silane: m.p. $-185°$, b.p. $-112°$ (760 mm), d $(-185°)$ = 0.68 (151).
SiFClBr$_2$	Fluorochlorodibromosilane: b.p. 59.5° (760 mm), m.p. $-99.3°$ (207).
SiFCl$_2$Br	Fluorodichlorobromosilane: b.p. 35.4° (760 mm), m.p. $-112.3°$ (207).
SiFBr$_3$	Fluorotribromosilane: b.p. 83.8° (760 mm), m.p. $-82.5°$ (173).
SiF$_2$Br$_2$	Difluorodibromosilane: m.p. $-66.9°$, b.p. 13.7° (760 mm) (173).
SiF$_3$Br	Trifluorobromosilane: m.p. $-70.5°$, b.p. $-41.7°$ (760 mm) (173).
SiBr$_4$	Tetrabromosilane: b.p. 153° (760 mm) (165).
CSiNOF$_3$	Trifluorosilicyl isocyanate: b.p. $-6°$ (757 mm) (580).
CSiNOCl$_3$	Trichlorosilicyl isocyanate: b.p. 152.0° (760 mm), m.p. $-35°$, d (25°) = 1.437, n (25°) = 1.4507 (512).
CH$_3$SiOCl$_3$	Methoxytrichlorosilane: b.p. 79.0°–79.5° (760 mm) (128).
CH$_3$SiF$_3$	Methyltrifluorosilane: b.p. $-30.2°$ (760 mm), m.p. $-72.8°$ (397); b.p. $-30°$ (760 mm) (432); b.p. $-28°$ (760 mm) (450).
CH$_3$SiF$_2$Cl	Methyldifluorochlorosilane: b.p. $-0.5°$ (760 mm), m.p. $-110.0°$ (397).
CH$_3$SiFCl$_2$	Methylfluorodichlorosilane: b.p. 29.5° (760 mm), m.p. $-98.7°$ (397).
CH$_3$SiCl$_3$	Methyltrichlorosilane: b.p. 66.2°–67.0° (765.8 mm) (95); b.p. 65.7° (760 mm), m.p. $-77.8°$ (397); b.p. 61°–69° (760 mm) (458).
CH$_3$SiBr$_3$	Methyltribromosilane: b.p. 133.5° (760 mm) (153); b.p. 133.5° (764 mm), d (20°/4°) = 2.253 (435).

CH_4SiCl_2	Methyldichlorosilane: m.p. $-93°$, d $(0°) = 0.93$ (98); b.p. $41.0°$ (749 mm), m.p. $-92.5°$, d $(27°/27°) = 1.105$ (267); b.p. $41°$ (760 mm) (354), b.p. $40.7°$ (760 mm) (649).
CH_3SiCl	Methylchlorosilane: m.p. $-134°$, d $(-80°) = 0.835$ (98).
CH_6Si	Methylsilane: b.p. $-57°$ (760 mm), m.p. $-156.5°$, d $(-57°) = 0.62$ (98).
$C_2SiN_2O_2F_2$	Difluorosilicyl diisocyanate: b.p. $68.5°-68.7°$ (757 mm), m.p. $-75°$, d $(20°) = 1.437$, n $= 1.3536$ (580).
$C_2SiN_2O_2Cl_2$	Dichlorosilicyl diisocyanate: b.p. $117.8°$ (760 mm), m.p. $-80°$, d $(25°) = 1.437$, n $(25°) = 1.4380$ (512).
$C_2H_3SiCl_3$	Vinyltrichlorosilane: b.p. $92°$ (760 mm), d $(27°/27°) = 1.264$ (357) b.p. $91.5°-92.5°$ (760 mm), d $(27°/27°) = 1.264$ (668).
$C_2H_3SiCl_5$	Methyltrichloromethyldichlorosilane: b.p. $109°$ (150 mm), m.p. $99°$ (451).
$C_2H_4SiCl_4$	β-Chloroethyltrichlorosilane: b.p. $152°$ (734 mm) (260).
$C_2H_4SiCl_4$	α-Chloroethyltrichlorosilane: b.p. $138°$ (734 mm) (260).
$C_2H_4SiCl_4$	Dichloromethylmethyldichlorosilane: b.p. $107.2°-107.8°$ (225 mm) (451).
$C_2H_5SiOCl_3$	Ethoxytrichlorosilane: b.p. $101.5°-102.0°$ (760 mm) (128), b.p. $102°-104°$ (760 mm) (655).
$C_2H_5SiF_3$	Ethyltrifluorosilane: b.p. $-4.4°$ (760 mm) (291); b.p. $4.2°$ (760 mm), m.p. $-113.3°$ (395).
$C_2H_5SiF_2Cl$	Ethyldifluorochlorosilane: b.p. $27.2°$ (760 mm) (395).
$C_2H_5SiFCl_2$	Ethylfluorodichlorosilane: b.p. $62.2°$ (760 mm) (395).
$C_2H_5SiCl_3$	Ethyltrichlorosilane: b.p. $97°-103°$ (760 mm) (2); b.p. $100°$ (760 mm) (126); b.p. $99.5°-100.5°$ (765.5 mm), d $(0°/4°) = 1.2666$, d $(10.1°/4°) = 1.2519$, d $(19.4°/4°) = 1.2388$, d $(29.7°/4°) = 1.2235$ (195); b.p. $97.9°$ (760 mm), m.p. $-105.6°$ (395).
$C_2H_5SiCl_3$	Chloromethylmethyldichlorosilane: b.p. $121.3°$ (760 mm) (451).
$C_2H_6SiO_2Cl_2$	Dimethoxydichlorosilane: b.p. $100.0°-100.5°$ (760 mm) (128).
$C_2H_6SiF_2$	Dimethyldifluorosilane: b.p. $2.7°$ (760 mm), m.p. $-87.5°$ (398); b.p. $3°$ (760 mm) (432); b.p. $2°$ (760 mm) (450).
C_2H_6SiFCl	Dimethylfluorochlorosilane: b.p. $36.4°$ (760 mm), m.p. $-85.1°$ (398).
$C_2H_6SiCl_2$	Dimethyldichlorosilane: b.p. $69.0°-70.2°$ (760 mm) (95); b.p. $70°$ (740 mm) (96); b.p. $70°$ (760 mm) (354); b.p. $70.0°$, m.p. $-76.1°$ (398).
$C_2H_6SiBr_2$	Dimethyldibromosilane: b.p. $112.3°$ (760 mm) (153, 435); d $(20°/4°) = 1.727$ (435).
C_2H_8Si	Dimethylsilane: m.p. $-149.4°$, b.p. $-20°$ (760 mm), d $(-80°) = 0.68$ (98).
C_2H_8Si	Ethylsilane: b.p. $-14°$ (632).
$C_3SiN_3O_3F$	Fluorosilicyl triisocyanate: b.p. $134.0°-134.4°$ (757 mm), m.p. $-29.2°$, d $(20°) = 1.456$, n $= 1.4161$ (580).
$C_3SiN_3O_3Cl$	Chlorosilicyl triisocyanate: b.p. $152°$ (760 mm), m.p. $-35°$, d $(25°) = 1.437$, n $(25°) = 1.4507$ (512).
$C_3H_5SiOCl_3$	Alloxytrichlorosilane: b.p. $112.0°-112.5°$ (760 mm) (128); b.p. $35.5°-36.0°$ (32 mm) (128, 357).
$C_3H_5SiOCl_3Br_2$	β-, γ-Dibromopropoxytrichlorosilane: b.p. $128°-129°$ (28 mm), d $(15°/15°) = 1.911$ (304).

$C_3H_5SiOCl_3$	β-, β'-Dichloro-i-propoxytrichlorosilane: b.p. 210° (760 mm), 92°-93° (12 mm), d (15°/15°) = 1.471 (304).
$C_3H_5SiCl_3$	Allyltrichlorosilane: b.p. 117.3° (760 mm), d (27°/27°) = 1.011 (357), b.p. 117°-118° (760 mm), d (27°/27°) = 1.211 (668); n (20°/D) = 1.451 (654).
$C_3H_6SiCl_2$	Allyldichlorosilane: b.p. 97° (760 mm), d (27°/27°) = 1.086 (357). b.p. 97.5°-98.5° (760 mm), d (27°/27°) = 1.086 (668).
$C_3H_6SiCl_2$	Methylvinyldichlorosilane: b.p. 93° (760 mm), d (27°/27°) = 1.085 (349), b.p. 92°-95° (760 mm), d (27°/27°) = 1.085 (668).
$C_3H_6SiCl_4$	α-Chloropropyltrichlorosilane: b.p. 157° (739 mm) (261).
$C_3H_6SiCl_4$	β-Chloropropyltrichlorosilane: b.p. 162° (729 mm) (261).
$C_3H_6SiCl_4$	γ-Chloropropyltrichlorosilane: b.p. 178.5° (732 mm) (261).
$C_3H_7SiFCl_2$	Propylfluorodichlorosilane: b.p. 88°-89° (760 mm) (396).
$C_3H_7SiFCl_2$	i-Propylfluorodichlorosilane: b.p. 84° (760 mm) (399).
$C_3H_7SiF_2Cl$	Propyldifluorochlorosilane: b.p. 55°-57° (760 mm) (396).
$C_3H_7SiF_2Cl$	i-Propyldifluorochlorosilane: b.p. 48.8° (760 mm) (399).
$C_3H_7SiF_3$	Propyltrifluorosilane: b.p. 24.9° (760 mm) (396).
$C_3H_7SiF_3$	i-Propyltrifluorosilane: b.p. 15.7° (760 mm), m.p. −127.6° (399).
$C_3H_7SiCl_3$	Propyltrichlorosilane: b.p. 123°-125° (760 mm) (78); b.p. 124.5°-125.0° (750 mm), d (0°/4°) = 1.2225, d (10°/4°) = 1.2096, d (20°/4°) = 1.1967, d (20.3°/4°) = 1.1833 (195), b.p. 122.7° (760 mm) (396).
$C_3H_7SiCl_3$	i-Propyltrichlorosilane: b.p. 119.4° (760 mm), m.p. −87.7° (399).
$C_3H_7SiCl_3$	α-Chloroethylmethyldichlorosilane: b.p. 135°-136° (760 mm) (357).
$C_3H_7SiCl_3$	β-Chloroethylmethyldichlorosilane: b.p. 156°-157° (760 mm) (357).
$C_3H_7SiCl_3$	Dichloromethyldimethylchlorosilane: b.p. 149.1°-149.9° (760 mm) (451).
$C_3H_7SiCl_3$	Dichloromethylmethylchlorosilane: b.p. 171.1°-172.8° (760 mm) (451).
$C_3H_8SiOCl_2$	Dimethyldichloromethylhydroxysilane: b.p. 89° (40 mm) (571).
$C_3H_8SiO_2Cl_2$	Ethoxymeethoxydichlorosilane: b.p. 128° (760 mm) (1).
$C_3H_8SiCl_2$	Dimethylchloromethylchlorosilane: b.p. 115°-116° (760 mm) (451).
C_3H_9SiNaO	Sodium trimethylsiloxide: m.p. 147°-150° + d (438).
$C_3H_9SiO_3Cl$	Trimethoxychlorosilane: b.p. 112.0°-112.5° (760 mm) (128).
C_3H_9SiF	Trimethylfluorosilane: b.p. 16.4° (760 mm), m.p. −74.3° (398); b.p. 17° (760 mm) (432), b.p. 15.4°-15.8° (734 mm) (653).
C_3H_9SiCl	Trimethylchlorosilane: b.p. 58.0°-58.2° (743 mm) (124); b.p. 57.3°-57.5° (757 mm) (355); b.p. 59.0° (760 mm), d (25°/4°) = 0.846, m.p. −40° (230); b.p. 57.0° (748 mm), 57.6°-57.7° (760 mm) (315); b.p. 57.0° (760 mm) (354). b.p. 57.3° (760 mm), m.p. −57.1° (398), b.p. 57°-60° (760 mm) (660); b.p. 58° (734 mm), n (20°/D) = 1.3884, d (20°) = 0.8581 (653).
C_3H_9SiBr	Trimethylbromosilane: b.p. 80°, d (25°) = 1.148 (349); b.p. 79.9° (754 mm), d (20°/4°) = 1.189 (435); b.p. 80°-81° (760 mm) (460).
$C_3H_{10}Si$	Trimethylsilane: b.p. 9°-11° (760 mm) (230).
$C_3H_{10}Si$	Propylsilane: b.p. 110°-116° (760 mm), n (20°/0°) = 1.3759, d (20°/4°) = 0.6434 (632).

$C_3H_{10}SiO$	Trimethylhydroxysilane: b.p. 98.5° (760 mm), n (20°/0°) = 1.3880, d (20°/4°) = 0.8112 (309).
$C_4SiN_4O_4$	Silicyl tetracyanate: b.p. 247.2° (760 mm), m.p. 34.5°, d (20°) = 1.414, n (20°) = 1.4646 (511).
$C_4SiN_4O_4$	Silicyl tetraisocyanate: b.p. 185.6° (760 mm), m.p. 26.0°, d (20°) = 1.409, 1.413, n (20°) = 1.4610 (511, 612, 580).
$C_4SiN_4S_4$	Silicyl tetra-i-thiocyanate: b.p. 313.0° (760 mm), m.p. 143.8°, d (20°/4°) = 1.409 (658).
$C_4H_3SiN_3O_4$	Methoxysilicyl triisocyanate: b.p. 168.4° (760 mm), d (20°/4°) = 1.313, n (20°) = 1.4287 (510).
$C_4H_3SiN_3S_3$	Methylsilicyl tri-i-thiocyanate: b.p. 266.8° (760 mm), m.p. 72.8°, d (20°/4°) = 1.304 (658).
$C_4H_6SiN_2O_4$	Dimethoxysilicyl diisocyanate: b.p. 152.1° (760 mm), d (20°/4°) = 1.208, n (20°) = 1.4028 (510).
$C_4H_6SiN_2S_2$	Dimethylsilicyl di-i-thiocyanate: b.p. 217.3° (760 mm), m.p. 18°, d (20°/4°) = 1.142, n (20°) = 1.5677 (658).
$C_4H_6SiCl_2$	Divinyldichlorosilane: b.p. 118°, d (27°/27°) = 1.081 (357), b.p. 118° (760 mm) (668).
$C_4H_7SiOCl_3$	Methallyltrichlorosilane: b.p. 141.0°–141.5° (760 mm), 53.0°–53.5° (32 mm) (128).
$C_4H_8SiCl_2$	Allylmethyldichlorosilane: b.p. 119° (760 mm), d (27°/27°) = 1.057 (349), b.p. 120° (760 mm), d (27°/27°) = 1.057 (668).
$C_4H_9SiNO_3S$	Trimethoxysilicyl thiocyanate: b.p. 170.5° (760 mm), d (20°) = 1.134, d (30°) = 1.1199, n (20°/D) = 1.4426 (496).
$C_4H_9SiNO_4$	Trimethoxysilicyl isocyanate: b.p. 137.6° (760 mm), d (20°/4°) = 1.123, n (20°) = 1.3839 (510).
C_4H_9SiNS	Trimethylsilicyl i-thiocyanate, b.p. 143.1° (760 mm), m.p. −32.8°, d(20°/4°) = 0.931, n(20°) = 1.4820 (658)
$C_4H_9SiOCl_3$	*t*-Butoxytrichlorosilane: b.p. 29°–30° (9 mm), d (20°) = 1.176 (587).
$C_4H_9SiOCl_3$	Butoxytrichlorosilane: b.p. 31°–45° (11 mm), d = 1.17 (591).
$C_4H_9SiSCl_3$	*t*-Butylmercaptotrichlorosilane: b.p. 174°–177° (306).
$C_4H_9SiFCl_2$	Butylfluorodichlorosilane: b.p. 116.1° (760 mm) (400).
$C_4H_9SiF_2Cl$	Butyldifluorochlorosilane: b.p. 84.0 (760 mm) (400).
$C_4H_9SiF_3$	Butyltrifluorosilane: b.p. 50°–52°, d = 1.006 (450); 52.4° (760 mm), m.p. −46.9° (400).
$C_4H_9SiCl_3$	Butyltrichlorosilane: b.p. 148°–149° (760 mm), d (0°/4°) = 1.1848, d (9.2°/4°) = 1.1740, d (18.8°/4°) = 1.1623, d (29.9°/4°) = 1.1487 (195); b.p. 148.5°–149.5° (760 mm), d (15°/4°) = 1.169 (236); b.p. 148.9° (760 mm) (400).
$C_4H_9SiCl_3$	*i*-Butyltrichlorosilane: b.p. 140.5°–141.5° (763 mm), d (0°/4°) = 1.180, d (20°/4°) = 1.154 (195); b.p. 138°–143° (760 mm), d (15°/4°) = 1.161 (419); b.p. 136° (630), b.p. 145°–146° (730 mm) (654).
$C_4H_9SiCl_3$	*t*-Butyltrichlorosilane: m.p. 98°–99°, b.p. 133° (740 mm) (506).
$C_4H_{10}SiO_2F_2$	Diethoxydifluorosilane: b.p. 83.0°–83.5° (755 mm) (130).
$C_4H_{10}SiO_2Cl_2$	Diethoxydichlorosilane: b.p. 136.0°–136.5° (760 mm), b.p. 51.5°–51.7° (32 mm) (128); b.p. 136° (760 mm) (554), b.p. 137°–138° (760 mm) (655).
$C_4H_{10}SiF_2$	Diethyldifluorosilane: b.p. 60.9° (760 mm), m.p. −78.7° (291).

$C_4H_{10}SiCl_2$ Diethyldichlorosilane: b.p. 128°–130° (760 mm), d (15°/4°) = 1.106 (66, 195); b.p. 131° (740 mm) (96); b.p. 130° (760 mm) (126); b.p. 129° (741 mm) (572).

$C_4H_{11}SiHgCl$ Chloromercurimethyltrimethylsilane: m.p. 76° (259).

$C_4H_{11}SiCl$ Chloromethyltrimethylsilane: b.p. 97.1° (734 mm), n (20°/D°) = 1.4180 (259).

$C_4H_{11}SiCl$ Diethylchlorosilane: b.p. 99° (741 mm), b.p. 99°–100° (760 mm) (649).

$C_4H_{11}SiCl$ Dimethylethylchlorosilane, b.p. 89.5°–90.5° (760 mm) (660)

$C_4H_{11}SiI$ Iodomethyltrimethylsilane: b.p. 139.5° (744 mm), n (20°/D) = 1.4917 (259).

$C_4H_{12}Si$ Tetramethylsilane: b.p. 26°–27° (760 mm), d (0°/4°) = 0.6688, d (10°/4°) = 0.6578, d (17°/4°) = 0.6497, d (21.9°/4°) = 0.6445 (195); b.p. 26°–27° (761.4 mm) (236); b.p. 30.5° (760 mm) (87); b.p. 26° (760 mm) (259, 354); b.p. 26°–27° (760 mm), d (18.7°/4°) = 0.6480 (419), b.p. 26.5° (760 mm), d (20°/4°) = 0.6480, n (20°) = 1.3591 (658).

$C_4H_{12}Si$ Diethylsilane: b.p. 56° (741 mm), n (20°/D) = 1.3921, d (20°) = 0.6843–0.6844 (582); b.p. 53°–57° (760 mm), n (20°/D) = 1.3918, d (20°/4°) = 0.6832 (632).

$C_4H_{12}Si$ Butylsilane: b.p. 55° (760 mm), n (20°/D) = 1.3929, d (20°/4°) = 0.6764 (632).

$C_4H_{12}SiO$ Trimethylmethoxysilane: b.p. 57° (760 mm), n (20°/D) = 1.3678 (309).

$C_4H_{12}SiO_2$ Diethyldihydroxysilane: m.p. 96° (314).

$C_4H_{12}SiO_4$ Tetramethoxysilane: b.p. 42.5°–43.0° (34 mm) (129); d (20°) = 1.0232, n (20°/D) = 1.3683 (335); b.p. 121°–122° (760 mm), d (23°/4°) = 1.032, d (27°/4°) = 1.010, d (47.5°/4°) = 0.993, d (60.5°/4°) = 0.973 (409); b.p. 121° (760 mm); d (20°/4°) = 1.023, n (20°) = 1.3683 (510).

$C_4H_{13}SiN$ Trimethylsilicyl methyl amine: b.p. 71° (755 mm), n (20°/D) = 1.3905, d (20°/4°) = 0.7395 (311).

$C_5H_{10}SiO_2Cl_2$ Alloxyethoxydichlorosilane: b.p. 66.0°–66.5° (32 mm) (128).

$C_5H_{10}SiO_4$ Methyldiacetoxysilane: b.p. 83°–84° (45 mm), d (25°/4°) = 1.0761 (583).

$C_5H_{10}SiCl_2$ Pentamethylenedichlorosilane: b.p. 169.8°–170.5° (760 mm), d (0°/4°) = 1.1779, d (10.1°/4°) = 1.1668, d (20°/4°) = 1.1560, d (30.1°/4°) = 1.1453 (195, 318); n (20.2°/D) = 1.46973 (318).

$C_5H_{11}SiOCl_3$ *t*-Amoxytrichlorosilane: b.p. 30°–32° (3 mm), d (20°) = 1.166 (587).

$C_5H_{11}SiF_3$ Amyltrifluorosilane: b.p. 77° (760 mm), d = 0.9923 (450).

$C_5H_{11}SiCl$ Allyldimethylchlorosilane: b.p. 111°–112° (760 mm), d (27°) = 0.022 (357).

$C_5H_{11}SiCl_3$ Amyltrichlorosilane: b.p. 107° (120 mm) (258); b.p. 166°–169° (760 mm) (630), b.p. 163°–167° (729 mm), 164°–165° (736 mm); n (20°/D) = 1.445, 1.4503 (654).

$C_5H_{11}SiCl_3$ *i*-Amyltrichlorosilane: b.p. 46° (9 mm), d = 1.066 (78); b.p. 56° (17 mm) (195).

$C_5H_{12}SiO_2$ Trimethylacetoxysilane: b.p. 30°–31° (35 mm), d (25°/4°) = 0.8961 (583).

$C_5H_{12}SiO_2$ Dimethyl-(trimethylene-1,3-dioxy)-silane: b.p. 121.7° (760 mm), d (20°/4°) = 0.9703, n (20°/D) = 1.4120 (631).

$C_5H_{12}SiO_2Cl_2$ *t*-Butoxymethoxydichlorosilane: b.p. 75°–76° (80 mm) (587).

$C_5H_{12}SiO_2Cl_2$ Methyldi-β-chloroethoxysilane: b.p. 93.5°–94.5° (15 mm), 70°–73.4° (4.5 mm), 97° (18 mm) (119); b.p. 96°–97° (18 mm), n (20°/D) = 1.4431, d (20°/4°) = 1.1643 (355).

$C_5H_{12}SiCl_2$ Ethylpropyldichlorosilane: m.p. 152.5°–154.5° (756.7 mm), d (0°/4°) = 1.0635, d (10°/4°) = 1.0532, d (20.7°/4°) = 1.0420, d (25°/4°) = 1.0375 (195).

$C_5H_{13}SiOCl$ β-Chloroethoxytrimethylsilane: b.p. 134.3° (760 mm), n (20°/D) = 1.4140, d (20°/4°) = 0.9443 (355); b.p. 131°–132° (748 mm) (119); b.p. 134° (760 mm), b.p. 55°–56° (50 mm) (120).

$C_5H_{13}SiCl$ α-Chloroethyltrimethylsilane: b.p. 117.8° (735 mm), n (20°/D) = 1.4242 (260).

$C_5H_{13}SiCl$ Diethylmethylchlorosilane: b.p. 119°–120° (760 mm) (660).

$C_5H_{14}Si$ Diethylmethylsilane: b.p. 77.2°–77.6° (648).

$C_5H_{14}Si$ Dimethylpropylsilane: b.p. 73°–74° (645).

$C_5H_{14}Si$ Ethyltrimethylsilane: b.p. 62.5°–63.5° (760 mm), d (0°/4°) = 0.7032, d (10.5°/4°) = 0.6931, d (20°/4°) = 0.6839, d (30°/4°) = 0.6736, d (41°/4°) = 0.6630, d (50.6°/4°) = 0.6533, d (60°/4°) = 0.6435 (195); b.p. 62.6°–63.4° (756.4 mm), (236); b.p. 25° (200 mm), d (20°/4°) = 0.6849, n (20°/D) = 1.3820 (258); b.p. 62.7°–63.5° (760 mm), d (20.2°/4°) = 0.6837 (419), b.p. 62° (734 mm), n (20°/D) = 1.3819, 1.3821 (650); b.p. 62.7°–63.2° (760 mm), n (20°/D) = 1.3820, d (20°) = 0.6842 (660).

$C_5H_{14}SiO$ Ethoxytrimethylsilane: b.p. 75° (745 mm), n (20°/D) = 1.3743, d (20°/4°) = 0.7573 (309); b.p. 99° (760 mm), (371); b.p. 75°–76° (760 mm) (373).

$C_5H_{14}SiO_3$ Ethyltrimethoxysilane: b.p. 126° (760 mm), d (0°) = 0.9747 (67), b.p. 123° (760 mm) (649).

$C_5H_{15}SiN$ Trimethylsilicyl ethyl amine: b.p. 90.1°–90.8° (760 mm), n (20°/D) = 1.3912 (311).

$C_5H_{16}SiN_2O_2$ *t*-Butoxymethoxydiaminosilane: b.p. 62°–65° (12 mm), n (20°/D) = 1.4130 (587).

$C_6H_4SiCl_4$ *p*-Chlorophenyltrichlorosilane: b.p. 105° (15 mm) (186).

$C_6H_4SiCl_3Br$ *p*-Bromophenyltrichlorosilane: b.p. 120°–125° (15 mm) (186).

$C_6H_5SiOCl_3$ Phenoxytrichlorosilane: b.p. 183°–186° (60 mm) (45).

$C_6H_5SiSCl_3$ Phenylmercaptotrichlorosilane: b.p. 110° (12 mm) (45).

$C_6H_5SiF_3$ Phenyltrifluorosilane: b.p. 101°–102° (760 mm), d = 1.201 (450).

$C_6H_5SiCl_3$ Phenyltrichlorosilane: m.p. 88°–89° (80); b.p. 197° (760 mm) (67, 408); b.p. 152°–153° (200 mm) (43); b.p. 197°–202° (760 mm) (17); b.p. 195°–200° (760 mm) (91, 126); b.p. 110° (50 mm) (91); b.p. 200.5°–201.5° (739.4 mm), d (0°/4°) = 1.3478, d (9.1°/4°) = 1.3372, d (18.8°/4°) = 1.3256, d (30.6°/4°) = 1.3120 (195), b.p. 201° (760 mm) (356).

$C_6H_6SiO_2$ Phenyloxohydroxysilane: m.p. 92° (74).

$C_6H_6SiCl_2$ Phenyldichlorosilane: b.p. 118°–119° (25 mm), 65.0°–65.3° (10 mm) (649).

C_6H_8Si Phenylsilane: b.p. 120° (760 mm), n (20°/D) = 1.5125, d (20°/4°) = 0.8681 (632).

$C_6H_{10}SiO_2Cl_2$ Dialloxydichlorosilane: b.p. 81.4°–81.8° (32 mm) (134); b.p. 80.5°–81.0° (32 mm) (128).

$C_6H_{10}SiO_2Cl_6$ Di-1,3-dichloro-2-propoxydichlorosilane: b.p. 140°–141° (0.28 mm), d (15°/15°) = 1.498 (304).

$C_6H_{10}SiO_2Cl_2Br_4$ Di-β,γ-dibromopropyldichlorosilane: b.p. 115°–120° (1 mm) (304).

$C_6H_{10}SiCl_2$ Diallyldichlorosilane: b.p. 82.0° (52 mm) (357), b.p. 165°–167° (760 mm), 83°–85° (50 mm) (668).

$C_6H_{11}SiCl_3$ Cyclohexyltrichlorosilane: b.p. 209°–211° (760 mm) (45); b.p. 199° (760 mm) (630).

$C_6H_{12}SiO_4$ Dimethyldiacetoxysilane: b.p. 44°–45° (3 mm), d (25°/4°) = 1.0485 (583).

$C_6H_{13}SiO_3Cl_3$ Tri-β-chloroethoxysilane: b.p. 117°–118° (2 mm) (119, 355); n (20°/D) = 1.4577, d (20°/D) = 1.2886 (355).

$C_6H_{13}SiCl_3$ Hexyltrichlorosilane; b.p. 127° (98 mm) (258).

$C_6H_{13}SiCl_3$ 2,3-Dimethyl-s-butyltrichlorosilane: b.p. 186°–187° (738 mm), n (20°/D) = 1.4631 (654).

$C_6H_{14}SiO_2$ Dimethyl-(tetramethylene-1,4-dioxy)-silane: b.p. 142° (760 mm), n (20°/D) = 1.4218 (631).

$C_6H_{14}SiO_2Cl_2$ t-Butoxyethoxydichlorosilane: b.p. 60°–61° (20 mm), d (20°) = 1.072 (587).

$C_6H_{14}SiO_2Cl_2$ Di-β-chloroethoxydimethylsilane: b.p. 213° (758 mm), n (20°/D) = 1.4420, d (20°/4°) = 1.135 (355); b.p. 212°–213° (758 mm) (119).

$C_6H_{14}SiO_2Br_2$ Di-β-bromoethoxydimethylsilane: b.p. 95° (3 mm), d (20°/4°) = 1.5425, n (20°/D) = 1.4780 (435).

$C_6H_{14}SiO_3$ Dimethyl-(2,2'-oxydiethoxy)-silane: b.p. 90° (50 mm), d (20°/4°) = 1.0452, n (20°/D) = 1.4331 (631).

$C_6H_{14}SiO_4$ Alloxytrimethoxysilane: b.p. 70.5°–70.8° (34 mm), n (20°/D) = 1.3919 (128, 129).

$C_6H_{14}SiFCl$ α-Chloroethyldiethylfluorosilane: b.p. 93° (113 mm), b.p. 107° (200 mm), b.p. 152° (760 mm), d (20°/4°) = 0.9955, n (20°/D) = 1.4208 (363), b.p. 149°–150° (760 mm), d (20°) = 0.9961 (651).

$C_6H_{14}SiFCl$ β-Chloroethyldiethylfluorosilane: b.p. 101° (77 mm), b.p. 126° (200 mm), b.p. 171° (760 mm), d (20°/4°) = 1.0100, n (20°/D) = 1.4277 (363).

$C_6H_{14}SiCl_2$ α-Chloroethyldiethylchlorosilane: b.p. 114° (100 mm), b.p. 134° (200 mm), b.p. 182° (760 mm), d (20°/4°) = 1.0401, n (20°/D) = 1.4561 (363), b.p. 178°–179°, 179°–181° (760 mm), n (20°/D) = 1.4553, d (20°) = 1.0399, 1.0385 (651).

$C_6H_{14}SiCl_2$ β-Chloroethyldiethylchlorosilane: b.p. 132° (100 mm), b.p. 153° (200 mm), b.p. 201° (760 mm), d (20°/4°) = 1.0552, n (20°/D) = 1.4636 (363).

$C_6H_{14}SiCl_2$ Ethyl-i-butyldichlorosilane: b.p. 169.5°–171.5° (758.2 mm), d (0°/4°) = 1.0394, d (10°/4°) = 1.0334, d (20°/4°) = 1.0235, d (25°/4°) = 1.0184 (195); b.p. 168°–170° (758 mm), d (15°/4°) = 1.028, d (20°/4°) = 1.4404 (419).

$C_6H_{14}SiCl_2$ Dipropyldichlorosilane: b.p. 173.5°–177.5° (760 mm), d (15°/4°) = 1.035 (195).

$C_6H_{14}SiCl_2$ Amylmethyldichlorosilane: b.p. 164°–168° (760 mm) (630).

$C_6H_{14}SiCl_2$ 2-Pentylmethyldichlorosilane: b.p. 100° (760 mm) (630).

$C_6H_{14}SiClBr$ Diethyl-α-chloroethylbromosilane: b.p. 194°–196° (760 mm), 105°–106° (46 mm), n (20°/D) = 1.4762, 1.4784, d (20°) = 1.2661 (651).

$C_6H_{15}SiOCl$ α-Chloroethyldiethylhydroxysilane: b.p. 150° (200 mm), b.p. 195° (760 mm), d (20°/4°) = 1.0238, n (20°/D) = 1.4067 (363).

$C_6H_{15}SiOCl$ Dimethylbutoxychlorosilane: b.p. 142° (741 mm) (132).

$C_6H_{15}SiOCl$ Diethylethoxychlorosilane: b.p. 148° (760 mm) (572).

$C_6H_{15}SiO_2Cl$ Diethoxyethylchlorosilane: b.p. 151° (66).

$C_6H_{15}SiO_3Cl$ Triethoxychlorosilane: b.p. 156.0°–156.5° (760 mm), b.p. 68.5°–69.0° (32 mm) (128); b.p. 155°–157° (760 mm) (554), b.p. 156.5° (760 mm) (655).

$C_6H_{15}SiO_3F$ Triethoxyfluorosilane: b.p. 133.0°–133.5° (760 mm) (130).

$C_6H_{15}SiF$ Triethylfluorosilane: b.p. 109° (745 mm), n (25°/D) = 1.3900, d (25°/4°) = 0.8354 (171); b.p. 110° (760 mm) (410), b.p. 109°–110° (760 mm), d (20°) = 0.8380 (651).

$C_6H_{15}SiCl$ Triethylchlorosilane: b.p. 143.5° (760 mm), d (0°) = 0.9249 (66); b.p. 144° (735 mm), n (20°/D) = 1.4314, d (20°/4°) = 0.8967 (363); b.p. 145° (729 mm), n (20°/D) = 1.4311 (438); b.p. 144° (729 mm) (582), b.p. 144° (760 mm) (660); b.p. 144°–145° (760 mm), d (20°) = 0.8974 (651).

$C_6H_{15}SiBr$ Triethylbromosilane: b.p. 66.5° (24 mm) (192), b.p. 79° (734 mm) (653); b.p. 162°–163° (760 mm), 78°–79° (45 mm), n (20°/D) = 1.4563, 1.4561, d (20°) = 1.1403 (651).

$C_6H_{15}SiI$ Triethyliodosilane: b.p. 106.5° (734 mm) (653).

$C_6H_{16}Si$ Diethyldimethylsilane: b.p. 107° (760 mm), d (0°) = 0.7510 (66); b.p. 63°–67° (760 mm) (87); b.p. 95.7°–96.2° (760 mm), d (0°/4°) = 0.7348, d (11°/4°) = 0.7247, d (20°/4°) = 0.7168, d (30°/4°) = 0.7084, d (73.1°/4°) = 0.6687, d (81.2°/4°) = 0.6610, d (91.°/4°) = 0.6511 (195); b.p. 95.5°–96.0° (759.8 mm) (236); b.p. 95.7°–96.2° (760 mm), d (24.8°/4°) = 0.7130 (195).

$C_6H_{16}Si$ Propyltrimethylsilane: b.p. 89.5°–89.8° (760 mm), d (0°/4°) = 0.7196, d (11.1°/4°) = 0.7099, d (21.3°/4°) = 0.7005, d (30.8°/4°) = 0.6920, d (43.4°/4°) = 0.6803, d (54.1°/4°) = 0.6702, d (75.5°/4°) = 0.6495, d (85.2°/4°) = 0.6399 (195); b.p. 40° (200 mm), d (20°/4°) = 0.7020, n (20°/D) = 1.3929 (258); b.p. 89.3°–89.6° (759.8 mm) (236); b.p. 89.5°–89.8° (760 mm), d (25°/4°) = 0.6973 (419), b.p. 89° (729 mm), n (20°/D) = 1.3930 (650).

$C_6H_{16}Si$ Triethylsilane: b.p. 107° (760 mm), d (0°/4°) = 0.751 (349); b.p. 107° (733 mm), n (20°/D) = 1.4117, d (20°) = 0.7302 (582); b.p. 106.8°–107.2° (645).

$C_6H_{16}Si$ Dipropylsilane: b.p. 23° (760 mm), n (20°/D) = 1.4112, d (20°/4°) = 0.7194 (632).

$C_6H_{16}SiNCl$ Diethyl-α-chloroethylaminosilane: b.p. 93° (38 mm), n (20°/D) = 1.4570, d (20°) = 0.9604 (651).

$C_6H_{16}SiO$ Triethylhydroxysilane: b.p. 70.5° (18.5 mm), d (20°/4°) = 0.8647, n (20°/D) = 1.43634 (192); b.p. 77.5° (28 mm), n (20°/D) = 1.4329, d (20°/D) = 0.8638 (438).

$C_6H_{16}SiO$ Di-*i*-propylhydroxysilane: b.p. 64°–65° (4 mm), b.p. 74°–75° (6 mm), d (20°/4°) = 0.8435, n (20°/D) = 1.4350 (522).

C$_6$H$_{16}$SiO$_2$	Diethoxydimethylsilane: b.p. 114° (740 mm) (255, 258).
C$_6$H$_{16}$SiO$_2$	Diethyldimethoxysilane: b.p. 130° (760 mm) (649).
C$_6$H$_{16}$SiO$_3$	Triethoxysilane: b.p. 132°–135° (760 mm), d (25°/4°) = 0.8745 (642).
C$_6$H$_{16}$SiO$_4$	Triethoxyhydroxysilane: b.p. 154.9° (760 mm), d (0°/4°) = 0.8709 (66).
C$_6$H$_{17}$SiN	Triethylaminosilane: b.p. 134° (760 mm), n (20°/D) = 1.4267 (651).
C$_6$H$_{18}$SiN$_2$O$_2$	*t*-Butoxyethoxydiaminosilane: b.p. 63°–66° (9 mm), d (20°) = 0.961, n (20°/D) = 1.4185 (587).
C$_7$H$_6$SiOCl$_3$Br	3-Bromo-6-methoxyphenyltrichlorosilane: b.p. 130°–140° (760 mm) (126).
C$_7$H$_6$SiCl$_4$	α-Chlorobenzyltrichlorosilane: b.p. 162° (75 mm) (260).
C$_7$H$_7$SiO$_2$Cl$_3$	Guaiacoxytrichlorosilane: b.p. 134°–136° (30 mm), d (18°/18°) = 1.3677 (310).
C$_7$H$_7$SiCl$_3$	Benzyltrichlorosilane: b.p. 94°–98° (11 mm), d = 1.2834 (78)
C$_7$H$_7$SiCl$_3$	*p*-Tolyltrichlorosilane: b.p. 210°–215° (760 mm), b.p. 125° (50 mm) (31).
C$_7$H$_8$SiO$_2$Cl$_2$	Methoxyphenoxydichlorosilane: b.p. 216° (752 mm) (1).
C$_7$H$_8$SiCl$_2$	Methylphenyldichlorosilane: b.p. 82.5° (13 mm) (96).
C$_7$H$_8$SiCl$_2$	Benzyldichlorosilane: b.p. 48° (2 mm) (649).
C$_7$H$_{12}$SiO	2-Furyltrimethylsilane: b.p. 124°–125° (750 mm), n (20°/D) = 1.4470, d (20°/4°) = 0.880 (699).
C$_7$H$_{12}$SiO$_6$	Methyltriacetoxysilane: b.p. 94°–95° (9 mm), d (25°/4°) = 1.677 (583).
C$_7$H$_{12}$SiS	2-Thienyltrimethylsilane: b.p. 159°–160° (748 mm), n (20°/D) = 1.4966, d (20°/4°) = 0.945 (699).
C$_7$H$_{15}$SiO$_3$Cl	Alloxydiethoxychlorosilane: b.p. 85.5°–86.0° (32 mm) (128).
C$_7$H$_{15}$SiO$_3$Cl$_3$	Methyltri-β-chloroethoxysilane: b.p. 137° (6 mm), n (20°/D) = 1.4562, d (20°/4°) = 1.257 (355); b.p. 136°–137° (119).
C$_7$H$_{15}$SiO$_3$Br$_3$	Methyltri-β-bromoethoxysilane: b.p. 131° (1 mm) (119); b.p. 130°–131° (1 mm), d (20°/4°) = 1.7635, n (20°/D) = 1.5001 (435).
C$_7$H$_{16}$Si	Dimethylpentamethylenesilane: b.p. 133°–134° (752.9 mm), d (0°/4°) = 0.8210, d (10.6°/4°) = 0.8120, d (20°/4°) = 0.8039, d (29.8°/4°) = 0.7959, d (30.9°/4°) = 0.7858, d (41.2°/4°) = 0.7773, d (67.1°/4°) = 0.7632, d (80.5°/4°) = 0.7512 (195, 318); n (20°/D) = 1.43940 (318); b.p. 133°–134° (760 mm), d (20.1°/4°) = 0.8038 (419).
C$_7$H$_{16}$SiO$_2$Cl$_2$	*t*-Butoxy-*i*-propoxydichlorosilane: b.p. 64°–66° (17 mm), d (20°) = 1.023 (587).
C$_7$H$_{16}$SiO$_4$	Methalloxytrimethoxychlorosilane: b.p. 83.0°–84.5° (34 mm), n (20°/D) = 1.4003 (128, 129).
C$_7$H$_{17}$SiO$_2$Cl	*i*-Butylethoxymethoxychlorosilane: b.p. 155° (760 mm) (1).
C$_7$H$_{17}$SiCl	α-Chloroethyldiethylmethylsilane: b.p. 125° (200 mm), 172° (760 mm), d (20°/4°) = 0.9036, n (20°/D) = 1.4452 (363).
C$_7$H$_{18}$Si	Butyltrimethylsilane: b.p. 115.3°–115.5° (758.2 mm), d (0°/4°) = 0.7353, d (11.6°/4°) = 0.7255, d (17°/4°) = 0.7208, d (25.3°/4°) = 0.7137, d (37°/4°) = 0.7035, d (66.1°/4°) = 0.6775, d (84.8°/4°) = 0.6604 (195); b.p. 115.0°–115.2° (758.2 mm) (236); b.p. 74° (200 mm), d (20°/4°) = 0.7181, n (20°/D) = 1.4030 (258); b.p. 115.3°–115.5° (760 mm), d (24.8°/4°) = 0.7141 (419).

$C_7H_{18}Si$	i-Butyltrimethylsilane: b.p. 108.1°–108.5° (757.2 mm), d (0°/4°) = 0.7330, d (12.6°/4°) = 0.7224, d (18.4°/4°) = 0.7175, d (25.1°/4°) = 0.7116, d (35.3°/4°) = 0.7029, d (29.9°/4°) = 0.6899 (195).
$C_7H_{18}Si$	Dipropylmethylsilane: b.p. 126.8–127.2 (645).
$C_7H_{18}Si$	t-Butyltrimethylsilane: m.p. 75°–77°, b.p. 103° (740 mm) (506).
$C_7H_{18}Si$	Dimethylethylpropylsilane: b.p. 120.0°–122.0° (759.2 mm) (236); b.p. 120°–122.4° (758.2 mm), d (0°/4°) = 0.7467, d (12.1°/4°) = 0.7368, d (17.6°/4°) = 0.7322, d (24.6°/4°) = 0.7263, d (41.7°/4°) = 0.7121, d (60.0°/4°) = 0.6956, d (81.2°/4°) = 0.6777 (195); b.p. 120.4°–122.4° (760 mm), d (25.2°/4°) = 0.7259 (410).
$C_7H_{18}Si$	Methyltriethylsilane: b.p. 84° (200 mm), d (20°/4°) = 0.7437, n (20°/D) = 1.4160 (258); b.p. 119°–123° (760 mm), d (20°/4°) = 0.7420 (338); b.p. 126° (760 mm), n (20°/D) = 1.4150 (438), b.p. 126° (760 mm), n (20°/D) = 1.4160 (650).
$C_7H_{18}SiO$	Butoxytrimethylsilane: b.p. 124° (760 mm), n (20°/D) = 1.3925, d (20°/4°) = 0.7774 (309).
$C_7H_{18}SiO_3$	Methyltriethoxysilane: b.p. 141°–145° (760 mm) (255, 258).
$C_7H_{19}SiN$	Trimethylsilicyl diethyl amine: b.p. 126.1°–126.4° (750 mm), n (20°/D) = 1.4112 (311).
$C_7H_{20}SiN_2O_2$	t-Butoxy-i-propoxydiaminosilane: b.p. 64°–66° (8 mm), d (20°) = 0.934, n (20°/D) = 1.4170 (587).
$C_8H_{10}SiCl_2$	Ethylphenyldichlorosilane: b.p. 100° (13 mm) (96); b.p. 230°–231° (760 mm), b.p. 155°–156° (100 mm) (2); b.p. 225°–235° (760 mm) (126); b.p. 228°–230° (760 mm) (195, 268); d (15°/4°) = 1.159 (195).
$C_8H_{12}SiO_2$	Ethylphenyldihydroxysilane: m.p. 70° (20).
$C_8H_{12}SiO_8$	Tetraacetoxysilane: m.p. 110° (583).
$C_8H_{14}SiO_2Cl_2$	Dimethallyoxydichlorosilane: b.p. 88.5°–89.0° (20 mm) (128).
$C_8H_{14}SiO_4$	Diallyloxyethyleneoxysilane: n (20°/D) = 1.4391 (128).
$C_8H_{14}SiO_6$	Ethyltriacetoxysilane: b.p. 97°–99° (4 mm), d (25°/4°) = 1.1426 (583).
$C_8H_{15}SiO_3Cl$	Diallyloxyethoxychlorosilane: b.p. 98°–99° (32 mm) (128).
$C_8H_{16}SiO_4$	Diallyloxydimethoxysilane: b.p. 94.5°–95.0° (34 mm), n (20°/D) = 1.4110 (128, 129).
$C_8H_{16}SiO_4$	Diethyldiacetoxysilane: b.p. 70°–72° (4 mm), d (25°/4°) = 1.0190 (583).
$C_8H_{16}SiO_4Cl_4$	Tetra-β-chloroethoxysilane: b.p. 184° (7 mm), b.p. 153°–154° (2 mm) (120, 355); n (20°/D) = 1.4641, d (20°/4°) = 1.344 (355); b.p. 159°–162° (2 mm), b.p. 175°–177° (5 mm) (119), b.p. 174° (5 mm), 188° (10 mm), 205° (20 mm), 227° (50 mm) (661).
$C_8H_{17}SiCl_3$	Octyltrichlorosilane: b.p. 111° (28 mm) (258); b.p. 231–232 (728 mm) (633), b.p. 222°–223° (721 mm), 232° (727 mm), 231°–232° (731 mm), 219°–220° (731 mm); n (20°/D) = 1.4480, 1.4478, 1.4532 (654).
$C_8H_{18}Si$	Triethylvinylsilane: b.p. 146° (760 mm), d (20°/20°) = 0.7767, n (20°/D) = 1.4330 (212).
$C_8H_{18}SiO_2$	Acetoxytriethylsilane: b.p. 168° (760 mm), d (0°/4°) = 0.9030 (66); b.p. 167° (726 mm) (438).
$C_8H_{18}SiO_2Cl_2$	s-Butoxy-t-butoxydichlorosilane: b.p. 72°–73° (9 mm), d (20°) = 1.040 (587).

$C_8H_{18}SiO_2Cl_2$ Di-t-butoxydichlorosilane: b.p. 70° (15 mm), d (20°) = 1.034 (587).

$C_8H_{18}SiO_2Cl_2$ Dibutoxydichlorosilane: b.p. 82.0°–84.5° (7.5 mm), b.p. 103° (20 mm), d = 1.05 (591).

$C_8H_{18}SiO_2Cl_2$ Butoxy-t-butoxydichlorosilane: b.p. 73°–74° (9 mm), d (20°) = 1.040 (587).

$C_8H_{18}SiO_4$ Dimethyl-(2,2'-ethylenedioxydiethoxy)-silane: b.p. 96 (9 mm), d (20°/4°) = 1.0704, n (20°/D) = 1.4487 (631).

$C_8H_{18}SiF_2$ Dibutyldifluorosilane: b.p. 153.9°–154.1° (760 mm), d (26.5°/4°) = 0.9048 (450).

$C_8H_{18}SiCl_2$ $\beta\beta$-Dichloroethyltriethylsilane: m.p. 208° (87).

$C_8H_{19}SiCl$ Chloroethyltriethylsilane: b.p. 185° (760 mm) (61).

$C_8H_{19}SiCl$ α-Chloroethyltriethylsilane: b.p. 72°–73° (9 mm), d (17°/17°) = 0.9143, n (17°/D) = 1.4538 (212).

$C_8H_{19}SiCl$ β-Chloroethyltriethylsilane: b.p. 80°–82° (9 mm), d (17°/17°) = 0.9158, n (17°/D) = 1.4562 (212).

$C_8H_{20}Si$ Amyltrimethylsilane: b.p. 95° (200 mm), d (20°/4°) = 0.7313, n (20°/D) = 1.4096 (258).

$C_8H_{20}Si$ i-Amyltrimethylsilane: b.p. 131.5°–132.5° (758.5 mm), d (0°/4°) = 0.7448, d (12°/4°) = 0.7349, d (16.2°/4°) = 0.7313, d (27°/4°) = 0.7222, d (43.3°/4°) = 0.7084, d (62.3°/4°) = 0.6920, d (81.3°/4°) = 0.6752 (195); b.p. 131°–132° (759.4 mm) (236); b.p. 131.5°–132.5° (760 mm), d (24.9°/4°) = 0.7240 (419).

$C_8H_{20}Si$ i-Butylethyldimethylsilane: b.p. 137°–139° (758.5 mm), d (0°/0°) = 0.7802 (236); b.p. 137.5°–139.5° (760 mm), d (0°/4°) = 0.7583, d (11.8°/4°) = 0.7488, d (19.2°/4°) = 0.7428, d (28.1°/4°) = 0.7316, d (48.2°/4°) = 0.7193, d (63.4°/4°) = 0.7048, d (79.5°/4°) = 0.6929 (195); b.p. 137.5°–139.5° (760 mm), d (25°/4°) = 0.7377 (419).

$C_8H_{20}Si$ Dimethyldipropylsilane: b.p. 141°–142° (757.8 mm), d (0°/4°) = 0.7555, d (11.8°/4°) = 0.7461, d (17.6°/4°) = 0.7414, d (27.4°/4°) = 0.7337, d (48.3°/4°) = 0.7168 (195).

$C_8H_{20}Si$ Tetraethylsilane: b.p. 150.0°–151.0° (760 mm), n (20°/D) = 1.4234, d (20°/4°) = 0.7660 (422); b.p. 152.8°–153.2° (759.5 mm), d (0°/0°) = 0.7802 (236); b.p. 108° (200 mm), d (20°/4°) = 0.7662, n (20°/D) = 1.4268 (258); b.p. 153.7° (758.7 mm), d (0°/4°) = 0.7812, d (10°/4°) = 0.7736, d (19.6°/4°) = 0.7662, d (29.5°/4°) = 0.7596, d (40.6°/4°) = 0.7501, d (51.7°/4°) = 0.7414, d (61.6°/4°) = 0.7340, d (73.3°/4°) = 0.7244, d (81.7°/4°) = 0.7178, d (91.6°/4°) = 0.7096 (195); b.p. 152° (760 mm) (88); b.p. 151.0°–151.5° (760 mm) (87); b.p. 150° (760 mm), d (20°/4°) = 0.8311 (66); b.p. 153° (759 mm), d (20°/4°) = 0.7660, d (12°/4°) = 0.7563, d (54°/4°) = 0.7386, d (66°/4°) = 0.7305, d (96°/4°) = 0.7402, d (122.5°/4°) = 0.6857 (409); b.p. 150°–154° (760 mm) (69, 413); b.p. 150°–154° (760 mm) (554); b.p. 152.5° (760 mm), d (0°) = 0.7657 (572), b.p. 152°–154° (734 mm), n (20°/D) = 1.4259, 1.4245 (650).

$C_8H_{20}SiO$ Hydroxyethyltriethylsilane: b.p. 190° (760 mm) (87, 221).

$C_8H_{20}SiO$ Ethoxytriethylsilane: b.p. 153° (760 mm) (66); b.p. 154°–155° (760 mm), d (26.5°/4°) = 0.8310, n (26.5°/D) = 1.4914 (362); b.p.

$C_8H_{20}SiO_2$	Diethoxydiethylsilane: b.p. 112° (760 mm) (96); b.p. 155.5° (760 mm), d (0°) = 0.8752 (572), b.p. 156°–157° (760 mm) (649).
$C_8H_{20}SiO_2$	Dimethylbutoxyethoxysilane: b.p. 155° (760 mm), d (20°/4°) = 0.8426, n (20°/D) = 1.3949 (631).
$C_8H_{20}SiO_2$	*d*-Dimethyl-*s*-butoxyethoxysilane: b.p. 144.6° (760 mm), d (20°/4°) = 0.8328, n (20°/D) = 1.3930 (631).
$C_8H_{20}SiO_2$	*dl*-Dimethyl-*s*-butoxyethoxysilane: b.p. 144.6° (760 mm), d (20°/4°) = 0.8432, n (20°/D) = 1.3932 (631).
$C_8H_{20}SiO_3$	Ethyltriethoxysilane: b.p. 158.5° (760 mm), d (0°) = 0.9207 (572), b.p. 158°–160° (760 mm) (649).
$C_8H_{20}SiO_4$	Tetraethoxysilane: b.p. 95.8°–97.5° (70 mm) (306); b.p. 67.5°–68.0° (18 mm), b.p. 78.5°–81.0° (34 mm), n (20°/D (= 1.3835 (129); b.p. 77.0°–77.5° (32 mm) (132); d (20°/4°) = 0.9283, n (20°/D) = 1.3832 (335); b.p. 165.3°–165.8° (760 mm), d (17°/4°) = 0.933, d (39.5°/4°) = 0.904, d (51.5°/4°) = 0.887, d (64.4°/4°) = 0.876 (409); b.p. 166.5° (760 mm), d (0°) = 0.9676 (572); b.p. 168.1° (760 mm), m.p. −77°, d (20°/20°) = 0.9356, n (20°/D) = 0.3852 (586).
$C_8H_{20}SiO_4$	Di-*t*-butoxydihydroxysilane: m.p. 99°–101° (586).
$C_8H_{22}SiN_2O_2$	Butoxy-*t*-butoxydiaminosilane: b.p. 66°–68° (3 mm), d (20°) = 0.939, n (20°/D) = 1.4260 (587).
$C_8H_{22}SiN_2O_2$	*s*-Butoxy-*t*-butoxydiaminosilane: b.p. 92°–95° (17 mm), d (20°) = 0.928, n (20°/D) = 1.4210 (587).
$C_8H_{22}SiN_2O_2$	Di-*t*-butoxydiaminosilane: b.p. 70°–72° (10 mm), d (20°) = 0.928, n (20°/D) = 1.4192 (587).
$C_9H_{12}SiCl_2$	Benzylethyldichlorosilane: b.p. 169° (100 mm) (3).
$C_9H_{13}SiO_3Cl$	Ethoxymethoxyphenoxychlorosilane: b.p. 241° (760 mm) (1).
$C_9H_{13}SiO_3Br$	*p*-Bromophenyltrimethyoxysilane: b.p. 136° (13.5 mm), d (16.5°/4°) = 1.3535, n (16.5°/D) = 1.5121 (192).
$C_9H_{13}SiCl$	*p*-Chlorophenyltrimethylsilane: b.p. 119°–120° (50 mm), d (20°/4°) = 1.0282, n (20°/D) = 1.5128 (421).
$C_9H_{13}SiBr$	*p*-Bromophenyltrimethylsilane: b.p. 146°–148° (50 mm), d (20°/4°) = 1.2197, n (20°/D) = 1.5302 (421).
$C_9H_{14}Si$	Phenyltrimethylsilane: b.p. 171.1°–171.3° (760 mm), d (24.7°/4°) = 0.8651 (419); b.p. 171.1°–171.3 (758.4 mm), d (0°/4°) = 0.8858, d (10.6°/4°) = 0.8770, d (21.2°/4°) = 0.8681, d (30°/4°) = 0.8606, d (41.2°/4°) = 0.8511, d (54.7/4°), = 0.8421, d (66.1°/4°) = 0.8296 (90, 195).
$C_9H_{14}SiO$	Ethylmethylphenylhydroxysilane: b.p. 115° (17 mm) (349).
$C_9H_{14}SiO_2$	Benzylethyldihydroxysilane: m.p. 100° (20).
$C_9H_{14}SiOS$	2-Acetyl-5-trimethylsilicylthiophene: b.p. 104°–105° (4 mm), n (20°/D) = 1.5289, d (20°/4°) = 1.028 (699).
$C_9H_{14}SiO_2$	2-Acetyl-5-trimethylsilicylfurane: b.p. 78.5°–79.0° (3 mm–4 mm), n (20°/D) = 1.4925, d (20°/4°) = 0.978 (699).
$C_9H_{15}SiO_3F$	Trialloxyfluorosilane: b.p. 99.0°–99.5° (32 mm) (130).
$C_9H_{15}SiO_3Cl$	Trialloxychlorosilane: b.p. 114.2°–114.8° (32 mm) (128, 134).
$C_9H_{15}SiO_3Cl_7$	Tri-1,3-dichloro-2-propoxychlorosilane: b.p. 196°–197° (0.36 mm), d (15°/15°) = 1.482 (304).
$C_9H_{16}SiO_2Cl_2$	Alloxycyclohexoxydichlorosilane: b.p. 127.0°–127.5° (32 mm) (128).

$C_9H_{16}SiO_6$ i-Propyltriacetoxysilane: b.p. 91°–92° (3 mm), d (25°/4°) = 1.1104 (583).

$C_9H_{19}SiCl_3$ 2-Nonyltrichlorosilane: b.p. 221°–222° (736 mm), n (20°/D) = 1.4500 (654).

$C_9H_{20}SiO_4$ Alloxytriethoxysilane: b.p. 93.5°–94.0° (34 mm), n (20°/D) = 1.3972 (128, 129); b.p. 92.5°–93.0° (32 mm), n (20°/D) = 1.3976 (130).

$C_9H_{21}SiF$ Tripropylfluorosilane: b.p. 17.5° (745 mm), n (25°/D) = 1.4107, d (25°/4°) = 0.8339 (171).

$C_9H_{21}SiCl$ Tri-i-propylchlorosilane: b.p. 198° (739 mm), b.p. 59° (8 mm), n (20°/D) = 1.4518, d (20°/4°) = 0.9008 (522).

$C_9H_{21}SiBr$ Tripropylbromosilane: b.p. 213° (760 mm) (70).

$C_9H_{22}Si$ Tripropylsilane: b.p. 170°–171° (760 mm), d (0°/4°) = 0.7723, d (15°/4°) = 0.8621 (70, 347); b.p. 109° (755 mm), d (26.5°/4°) = 0.744, n (25°/D) = 1.0492 (362); b.p. 169.5°–169.8° (645).

$C_9H_{22}Si$ Tri-i-propylsilane: b.p. 60°–61° (3.5 mm), b.p. 64°–65° (4 mm), n (20°/D) = 1.4358, d (20°/4°) = 0.7726 (522).

$C_9H_{22}Si$ Hexyltrimethylsilane: b.p. 117° (200 mm), d (20°/4°) = 0.7422, n (20°/D) = 1.4154 (258).

$C_9H_{22}Si$ Propyltriethylsilane: b.p. 127° (200 mm), d (20°/4°) = 0.7724, n (20°/D) = 1.4308 (258); b.p. 172.4°–172.8° (760 mm) d (0°/4°) = 0.7869, d (11.7°/4°) = 0.7783, d (17°/4°) = 0.7744, d (28.8°/4°) = 0.7655, d (49.5°/4°) = 0.7500, d (66.7°/4°) = 0.7365 (195); b.p. 172.4°–172.8° (760.4 mm), d (25°/4°) = 0.7864, n (20°/D) = 1.4308 (362); b.p. 172.4°–172.8° (760 mm), d (25.2°/4°) = 0.7862 (419).

$C_9H_{22}SiO$ Tripropylhydroxysilane: b.p. 205°–208° (760 mm) (70, 347).

$C_9H_{22}SiO_3$ Tripropoxysilane: b.p. 190°–194° (750 mm), d (25°/4°) = 0.882 (643).

$C_9H_{23}SiNO_3$ Di-t-butoxymethoxyaminosilane: b.p. 72°–73° (15 mm), d (20°) = 0.924, n (20°/D) = 1.405 (587).

$C_{10}H_7SiCl_3$ α-Naphthyltrichlorosilane: b.p. 165°–170° (22 mm), d = 1.3760 (78).

$C_{10}H_8SiO_2$ α-Naphthyloxohydroxysilane: m.p. 125°–130° (78); m.p. 239° (412); m.p. 138° (411).

$C_{10}H_{13}SiOCl_3$ Thymoxytrichlorosilane: b.p. 122°–124.5° (23 mm), d (15°/15°) = 1.3462 (310).

$C_{10}H_{13}SiOCl_3$ Carvacroxytrichlorosilane: b.p. 108°–111° (4 mm), d (20°/4°) = 1.1798 (310).

$C_{10}H_{15}SiO_2SCl$ Trimethylbenzylsilane p-sulfonyl chloride: m.p. 45.5°–46.5° (550).

$C_{10}H_{16}Si$ Benzyltrimethylsilane: b.p. 191.1°–191.3° (758.5 mm), d (0°/4°) = 0.8847, d (9.6°/4°) = 0.8766, d (19.5°/4°) = 0.8682, d (31.3°/4°) = 0.8584, d (41.4°/4°) = 0.8501, d (56.4°/4°) = 0.8389, d (65.0°/4°) = 0.8293, d (77.3°/4°) = 0.8196, d (90.4°/4°) = 0.8083 (195); b.p. 191.1°–191.3° (760 mm), d (24.7°/4°) = 0.8630 (419).

$C_{10}H_{16}Si$ Dimethylethylphenylsilane: b.p. 197.6°–198.6° (757.7 mm), d (0°/4°) = 0.8929, d (12.4°/4°) = 0.8834, d (18.8°/4°) = 0.8779, d (27.4°/4°) = 0.8713, d (40.7°/4°) = 0.8607, d (66.6°/4°) = 0.8404 (195); b.p. 197.6°–198.6° (760 mm), d (25.3°/4°) = 0.8729 (419).

$C_{10}H_{16}SiO$ Benzylethylmethylhydroxysilane: b.p. 115.0° (17 mm) (15).

$C_{10}H_{16}SiO$ Diethylphenylhydroxysilane: b.p. 165° (60 mm) (349).

$C_{10}H_{15}SiO_2SBr$ Trimethylbenzylsilane p-sulfonyl bromide: m.p. 60.0°–60.5° (550).

$C_{10}H_{17}SiNO_2S$ Trimethylbenzylsilane p-sulfonamide: m.p. 81.0°–81.5° (550).

$C_{10}H_{18}SiO_4$ Methoxytrialloxysilane: b.p. 116.0°–116.3° (34 mm), n (20°/D) = 1.4252 (128, 129).

$C_{10}H_{18}SiO_4S$ Trimethylbenzylsilane p-sulfonic acid monohydrate: m.p. 116°–116.5° (195, 550).

$C_{10}H_{19}SiOCl_3$ Menthoxytrichlorosilane: b.p. 112°–113° (9 mm), d (21°/4°) = 1.1439, n (21°/D) = 1.4615 (299).

$C_{10}H_{20}SiO_4$ Dialloxydiethoxysilane: b.p. 107.5°–108.0° (34 mm), n (20°/D) = 1.4098 (128, 129); b.p. 107.0°–107.5° (32 mm), n (20°/D) = 1.4097 (130).

$C_{10}H_{20}SiO_4$ Dicrotonoxydimethoxysilane: b.p. 114.5°–115.0° (34 mm), n (20°/D) = 1.4156 (128); b.p. 103.0°–103.5° (18 mm) (129).

$C_{10}H_{20}SiO_5$ Triethoxysilicyl methacrylate: n (25°/D) = 1.4048 (456).

$C_{10}H_{20}SiO_5S$ Trimethylbenzylsilane p-sulfonic acid dihydrate: m.p. 97°–114° (550).

$C_{10}H_{21}SiCl_3$ Decyltrichlorosilane: b.p. 183° (84 mm) (258).

$C_{10}H_{22}SiO_2$ β-Acetoxyethyltriethylsilane: b.p. 208°–214° (760 mm), (87), b.p. 204°–208° (760 mm) (61).

$C_{10}H_{22}SiO_2Cl_2$ Di-t-amoxydichlorosilane: b.p. 102° (17 mm), d (20°) = 1.027 (587).

$C_{10}H_{22}SiO_4$ Crotoxytriethoxysilane: b.p. 92.5°–93.0° (18 mm), n (20°/D) = 1.4051 (128); b.p. 92.5°–93.0° (34 mm), n (20°/D) = 1.4021 (130).

$C_{10}H_{22}SiF_2$ Diamyldifluorosilane: b.p. 193° (760 mm), d = 0.8972 (456).

$C_{10}H_{24}Si$ Heptyltrimethylsilane: b.p. 137° (200 mm), d (20°/4°) = 0.7506, n (20°/D) = 1.4201 (258).

$C_{10}H_{24}Si$ Butyltriethylsilane: b.p. 144° (200 mm), b.p. 192° (760 mm), n (20°/D) = 1.4348, d (20°/4°) = 0.7786 (258); b.p. 190.0°–191.5° (761.2 mm), d (27.6°/4°) = 0.7743, n (27.6°/D) = 1.4348 (362); d (11.9°/4°) = 0.7842, d (18.3°/4°) = 0.7792, d (26.5°/4°) = 0.7753, d (38°/4°) = 0.7648, d (54.3°/4°) = 0.7527, d (72.5°/4°) = 0.7293, d (88.5°/4°) = 0.7273 (195); b.p. 190.5°–191.5° (760 mm), (195, 419); d (25.4°/4°) = 0.7742 (419).

$C_{10}H_{24}Si$ i-Butyltriethylsilane: b.p. 186.6°–187.0° (761 mm), d (0°/4°) = 0.7944, d (11.7°/4°) = 0.7859, d (18.6°/4°) = 0.7808, d (26.6°/4°) = 0.7747, d (40.5°/4°) = 0.7648, d (54°/4°) = 0.7547, d (70.3°/4°) = 0.7426 (195); b.p. 186.6°–187.0° (760 mm), d (25°/4°) = 0.7758 (419).

$C_{10}H_{24}SiO_2$ Dibutoxydimethylsilane: b.p. 186°–188° (760 mm), b.p. 75° (10 mm), n (25°/D) = 1.4035, n (20°/D) = 1.4058, d (20°/4°) = 0.8434 (132).

$C_{10}H_{24}SiO_2$ d-Dimethyldi-s-butoxysilane: b.p. 173.6° (760 mm), d (20°/4°) = 0.8339, n (20°/D) = 1.4014 (631).

$C_{10}H_{24}SiO_2$ dl-Dimethyldi-s-butoxysilane: b.p. 174° (760 mm), d (20°/4°) = 0.8332, n (20°/D) = 1.4014 (631).

$C_{10}H_{24}SiO_3$ Butoxytriethoxysilane: b.p. 102.0°–102.5° (32 mm), n (20°/D) = 1.3934 (130).

$C_{10}H_{25}SiNO_3$	*t*-Butoxydi-*i*-propoxyaminosilane: b.p. 57°–60° (3 mm), d (20°) = 0.884, n (20°/D) = 1.4015 (587).
$C_{10}H_{26}SiN_2O_2$	Di-*t*-amoxydiaminosilane: b.p. 105°–110° (15 mm), d (20°) = 0.931, n (20°/D) = 1.4300 (587).
$C_{11}H_{17}SiCl$	Benzyldiethylchlorosilane: b.p. 155°–165° (15 mm) (15).
$C_{11}H_{17}SiCl$	Ethylphenylpropylchlorosilane: b.p. 178°–182° (760 mm) (2).
$C_{11}H_{18}SiO$	Ethylphenylpropylhydroxysilane: b.p. 250° (760 mm) (2).
$C_{11}H_{18}SiO$	Benzyldiethylhydroxysilane: b.p. 165° (40 mm) (15).
$C_{11}H_{18}SiO_2$	Methylphenyldiethoxysilane: b.p. 105°–110° (13 mm) (126).
$C_{11}H_{19}SiNO_2S$	Benzyltrimethylsilane p-N-methylsulfonamide: m.p. 86.4°–87.0° (550).
$C_{11}H_{20}SiO_4$	Ethoxytrialloxysilane: b.p. 120.5°–121.0° (32 mm), n (20°/D) = 1.4233 (131).
$C_{11}H_{20}SiO_5$	Furfuroxytriethoxysilane: b.p. 85.5°–86.5° (3 mm) (128).
$C_{11}H_{21}SiNO_3S$	Benzyltrimethylsilane p-sulfonic acid, methylammonium salt: m.p. 144°–172° (550).
$C_{11}H_{24}SiO_2$	Acetoxytripropylsilane: b.p. 212°–216° (760 mm), (70, 347).
$C_{11}H_{24}SiO_5$	Ethyl-β-carboxylatoethyltriethoxysilane: b.p. 115°–120° (14 mm) (303).
$C_{11}H_{26}Si$	Octyltrimethylsilane: b.p. 156° (200 mm), d (20°) = 0.7581, n (20°/D) = 1.4242 (258); b.p. 201.5° (733 mm), n (20°/D) = 1.4242 (633).
$C_{11}H_{26}Si$	Amyltriethylsilane: b.p. 162° (200 mm), d (20°/4°) = 0.7835, n (20°/D) = 1.4377 (258).
$C_{11}H_{26}Si$	*i*-Amyltriethylsilane: b.p. 204.1°–205.0° (756.3 mm), d (0°/4°) = 0.7954, d (11.6°/4°) = 0.7869, d (18.9°/4°) = 0.7816, d (30.2°/4°) = 0.7733, d (41°/4°) = 0.7655, d (55°/4°) = 0.7551, d (79.4°/4°) = 0.7370 (195); b.p. 204.1°–205.1° (760 mm), d (25.7°/4°) = 0.7766 (419).
$C_{11}H_{26}SiO$	Tri-*i*-propylethoxysilane: b.p. 198° or 200° (738 mm), n (20°/D) = 1.4560, d (20°/4°) = 0.8657 (522).
$C_{11}H_{26}SiO_4$	Triethoxyamoxysilane: b.p. 216°–225° (760 mm) (554).
$C_{11}H_{27}SiNO_3$	Di-*t*-butoxy-*i*-propoxyaminosilane: b.p. 83°–84° (17 mm), d (20°) = 0.819, n (20°/D) = 1.4053 (587).
$C_{12}H_8SiCl_2Br_2$	Di-*p*-bromophenyldichlorosilane: m.p. 60°, b.p. 238°–240° (21 mm) (186).
$C_{12}H_9SiCl_2Br$	*p*-Bromophenylphenyldichlorosilane: b.p. 199°–200° (14 mm), d (20°/4°) = 1.5005, n (20°/D) = 1.6092 (192).
$C_{12}H_{10}SiO$	Diphenyloxosilane: m.p. 109° (74); m.p. 188° (76).
$C_{12}H_{10}SiO_2Cl_2$	Diphenoxydichlorosilane: b.p. 167°–171° (13 mm) (83); b.p. 199.5°–202° (40 mm), b.p. 215°–218° (60 mm) (42).
$C_{12}H_{10}SiF_2$	Diphenyldifluorosilane: b.p. 158° (50 mm) (291); b.p. 246°–247° (760 mm), d = 1.155 (450).
$C_{12}H_{10}SiCl_2$	Diphenyldichlorosilane: b.p. 160° (10 mm) (96); b.p. 305.2° (760 mm) (356); b.p. 202°–204° (45 mm) (17); b.p. 230°–237° (90 mm) (71); b.p. 175°–185° (760 mm) (126); m.p. 160°, 188° (81); b.p. 170°–175° (19 mm) (458).
$C_{12}H_{10}SiBr_2$	Diphenyldibromosilane: b.p. 175°–183° (12 mm) (176).
$C_{12}H_{11}SiCl$	Diphenylchlorosilane: b.p. 140°–145° (7 mm) (649).

$C_{12}H_{12}SiO_2$ — Diphenyldihydroxysilane: m.p. 155° (96); m.p. 140° (81); m.p. 128°–132° (17); m.p. 139° (74); m.p. 201°–202°, b.p. 330°–340° (1 mm) (329).

$C_{12}H_{16}SiCl_2$ — Cyclohexylphenyldichlorosilane: b.p. 123°–125° (0.5 mm), b.p. 163°–165° (4 mm) (50).

$C_{12}H_{17}SiO_3Cl_3$ — Phenyltri-β-chloroethoxysilane: b.p. 158° (1 mm) (119, 355); n (20°/D) = 1.5077, d (20°/4°) = 1.2680 (355).

$C_{12}H_{18}SiO_2$ — Cyclohexylphenyldihydroxysilane: m.p. 123°–124° (50).

$C_{12}H_{19}SiNO_2$ — m-Nitrophenyltriethylsilane: b.p. 307° (760 mm) (51).

$C_{12}H_{19}SiO_3Br$ — p-Bromophenyltriethoxysilane: b.p. 149°–150° (12 mm), d (16.6°/4°) = 1.2276, n (15.4°/D) = 1.4925 (192).

$C_{12}H_{19}SiCl$ — p-Chlorophenyltriethylsilane: b.p. 261°–262° (760 mm), b.p. 137° (14.5 mm), d (9.6°/4°) = 1.0056, n (9.6°/D) = 1.52196 (186).

$C_{12}H_{19}SiCl$ — α-Chloroethyldiethylphenylsilane: b.p. 210° (200 mm), 274° (760 mm), d (20°/4°) = 1.0109, n (20°/D) = 1.5229 (363).

$C_{12}H_{19}SiCl$ — Benzylethylpropylchlorosilane: b.p. 174° (50 mm) (349).

$C_{12}H_{19}SiBr$ — p-Bromophenyltriethylsilane: b.p. 149° (14 mm), d (21°/4°) = 1.643, n (20°/D) = 1.53280 (186); b.p. 117°–118° (18 mm), d (20°/4°) = 0.8950, n (20°/7°) = 1.5067 (188, 192).

$C_{12}H_{19}SiI$ — p-Iodophenyltriethylsilane: b.p. 165° (13 mm) (186, 419); d (20°/4°) = 1.3304, n (20°/D) = 1.52756 (186); d (16°/4°) = 1.4432 (419).

$C_{12}H_{20}Si$ — Ethylmethylphenylpropylsilane: b.p. 228°–230° (760 mm) (2).

$C_{12}H_{20}Si$ — Tetrallylsilane, b.p. 102°–103° (15 mm), n (20°/D) = 1.4864, d (20°/4°) = 0.8353 (125).

$C_{12}H_{20}Si$ — Phenyltriethylsilane: b.p. 238° (760 mm), d (0°/4°) = 0.906 (349); b.p. 238.3°–238.5° (760 mm), d (26.3°/4°) = 0.8864 (362); b.p. 238.2°–238.5° (762.1 mm), d (0°/4°) = 0.9060, d (11.4°/4°) = 0.8976, d (18.7°/4°) = 0.8922, d (27.9°/4°) = 0.8852, d (40.3°/4°) = 0.8761, d (54°/4°) = 0.8659, d (77.4°/4°) = 0.8559, d (81.4°/4°) = 0.8485 (195); b.p. 237° (760 mm), d (0°/4°) = 1.0133, d (10°/4°) = 1.0055 (408); b.p. 238.3°–238.5° (760 mm), d (25.1°/4°) = 0.8874 (419), b.p. 168° (734 mm), n (20°/D) = 1.4900 (653).

$C_{12}H_{20}SiO$ — Benzylethylpropylhydroxysilane: b.p. 169°–170° (40 mm) (15).

$C_{12}H_{20}SiO_3$ — Phenyltriethoxysilane: b.p. 120° (15 mm) (126).

$C_{12}H_{20}SiO_4$ — Tetraalloxysilane: b.p. 134.5°–135.5° (34 mm) (129), b.p. 132.0°–132.5° (32 mm), n (20°/D) = 1.4336 (131).

$C_{12}H_{20}SiO_4S$ — Benzylethylpropylhydroxysilane p-sulfonic acid: m.p. 210°–212° (3).

$C_{12}H_{20}SiO_4Cl_8$ — Tetra-1.3-dichloro-2-propoxysilane: b.p. 213°–214° (0.2 mm), d (17°/17°) = 1.46099, n (17°/D) = 1.49640 (304).

$C_{12}H_{21}SiNO_3$ — p-Aminophenyltriethoxysilane: b.p. 145°–150° (14 mm) (126).

$C_{12}H_{21}SiO_3Cl$ — Tricrotoxychlorosilane: b.p. 122°–123° (20 mm) (128).

$C_{12}H_{21}SiO_3Cl$ — Cyclohexoxydialloxychlorosilane: b.p. 143°–144° (32 mm) (128).

$C_{12}H_{22}SiO_4$ — i-Propoxytrialloxysilane: b.p. 74.5°–75.0° (2 mm), n (20°/D) = 1.4204 (128).

$C_{12}H_{22}SiCl_2$ — Dicyclohexyldichlorosilane: b.p. 150° (4 mm) (45).

$C_{12}H_{23}SiNO_3S$ — Trimethylbenzylsilane, p-sulfonic acid, ethylammonium salt: m.p. 110.5°–111.5° (550).

$C_{12}H_{24}SiO_2$ — Dicyclohexyldihydroxysilane: m.p. 140°–145° (45); m.p. 164°–165° (50).

$C_{12}H_{24}SiO_3$ Ethyl β-triethoxysiloxycrotonate: b.p. 108°–110° (6 mm), n (20°/ D) = 1.4560, d (20°/4°) = 0.9590 (504).

$C_{12}H_{24}SiO_4$ Dialloxydi-i-propoxysilane: b.p. 57.5°–58.0° (2 mm), n (20°/D) = 1.4075 (128).

$C_{12}H_{24}SiO_4$ Dicrotoxydiethoxysilane: b.p. 115.5°–116.0° (18 mm), n (20°/D) = 1.4200 (128, 129).

$C_{12}H_{24}SiO_4Cl_4$ Tetra-β,β'-dichloro-i-propoxysilane: b.p. 244° (5 mm), 253° (10 mm), 259° (15 mm) (661).

$C_{12}H_{25}SiCl_3$ Dodecyltrichlorosilane: b.p. 120° (3 mm) (258); b.p. 162°–171° (18 mm) (520), b.p. 260°–275° (739 mm), n (20°/D) = 1.4581 (654).

$C_{12}H_{27}SiO_3F$ Tributoxyfluorosilane: b.p. 134.0°–134.5° (32 mm) (130).

$C_{12}H_{27}SiO_3Cl$ Tributoxychlorosilane: b.p. 126°–128° (10 mm), d = 0.97 (591).

$C_{12}H_{27}SiO_3Cl$ Tri-t-butoxychlorosilane: b.p. 76°–78° (5 mm), d (20°) = 0.937 (587); b.p. 65.5°–66.0° (306).

$C_{12}H_{27}SiS_3Cl$ Tri-t-butylmercaptochlorosilane: m.p. 71° (306).

$C_{12}H_{27}SiF$ Tributylfluorosilane: b.p. 224° (745 mm), n (25°/D) = 1.4250, d (25°/4°) = 0.8372 (171); b.p. 212°–214° (760 mm), d = 0.8465 (450).

$C_{12}H_{27}SiBr$ Tri-i-butylbromosilane: b.p. 245° (760 mm) (86, 349).

$C_{12}H_{28}Si$ Hexyltriethylsilane: b.p. 179° (200 mm), d (20°/4°) = 0.7880, n (20°/D) = 1.4400 (258).

$C_{12}H_{28}Si$ Tri-i-butylsilane: b.p. 204°–208° (760 mm) (86).

$C_{12}H_{28}Si$ Tetrapropylsilane: b.p. 213°–214° (760 mm), d (0°) = 0.7972, d (15°) = 0.7883 (70, 347); b.p. 212° (760 mm), (88); b.p. 213°–215° (751 mm), d (24.5°/4°) = 0.7869, d (40.5°/4°) = 0.7696, d (59.5°/4°) = 0.7560, d (75°/4°) = 0.7444, d (10.1°/4°) = 0.7254 (409).

$C_{12}H_{28}SiOS_3$ Tri-i-propylmercapto-i-propoxysilane: b.p. 183°–186° (3 mm), m.p. 55°–56° (306).

$C_{12}H_{28}SiO_3$ Tributoxysilane: b.p. 237°–238° (760 mm) (642).

$C_{12}H_{28}SiO_3$ Tri-i-butoxysilane: b.p. 224°–228° (751 mm), d (25°/4°) = 0.891 (642).

$C_{12}H_{28}SiO_4$ Tri-t-butoxyhydroxysilane: m.p. 65.5°–66.0° (306).

$C_{12}H_{28}SiO_4$ Dibutoxydiethoxysilane: b.p. 128.0°–128.5° (32 mm), n (20°/D) = 1.4010 (131).

$C_{12}H_{28}SiO_4$ Tetrapropoxysilane: b.p. 225°–227° (443).

$C_{12}H_{28}SiO_8$ Tetra-β-methoxyethoxysilane: b.p. 292° (740 mm), b.p. 183° (9 mm), n (20°/D) = 1.4213, d (20°/4°) = 1.0781, d (25°/4°) = 1.0680, viscosity (20°) = 0.0362, (25°) = 0.0288 (641).

$C_{12}H_{29}SiNO_3$ Tri-t-butoxyaminosilane: b.p. 82°–85° (10 mm), d (20°) = 0.883, n (20°/D) = 1.4060 (587).

$C_{12}H_{29}SiNO_3$ Butoxy-di-t-butoxyaminosilane: b.p. 113°–114° (15 mm), d (20°) = 0.901, n (20°/D) = 1.4149 (587).

$C_{13}H_{12}Si$ Diphenylmethylenesilane: b.p. 266°–267° (760 mm) (82).

$C_{13}H_{12}SiCl_2$ Benzylphenyldichlorosilane: b.p. 245° (100 mm) (349).

$C_{13}H_{14}SiO_2$ Benzylphenyldihydroxysilane: m.p. 104° (81).

$C_{13}H_{21}SiCl$ Benzylethyl-i-butylchlorosilane: b.p. 200° (100 mm) (349).

$C_{13}H_{22}Si$ Benzyltriethylsilane: b.p. 267°–269° (760 mm) (85).

$C_{13}H_{22}Si$ Benzylethylmethylpropylsilane: b.p. 250° (760 mm) (3).

$C_{13}H_{22}SiO$ Benzyl-*i*-butylethylhydroxysilane: b.p. 162°–164° (25 mm) (7).

$C_{13}H_{22}SiO_3$ *p*-Tolyltriethoxysilane: b.p. 137° (14 mm) (126).

$C_{13}H_{22}SiO_3$ Benzyltriethoxysilane: b.p. 248°, d = 0.9864 (78).

$C_{13}H_{22}SiO_3S$ Benzylethylmethylpropylsilane: p-sulfonic acid, m.p. 122°–123° (3).

$C_{13}H_{24}SiO_4$ *i*-Butoxytrialloxysilane: b.p. 85.5°–86.5° (3 mm) (128).

$C_{13}H_{24}SiO_4$ *s*-Butoxytrialloxysilane: b.p. 74.5°–75.0° (2 mm), n (20°/D) = 1.4242 (128).

$C_{13}H_{24}SiO_4$ *t*-Butoxytrialloxysilane: b.p. 73.0°–73.5° (2 mm), n (20°/D) = 1.4242 (128).

$C_{13}H_{24}SiO_4$ Methoxytricrotoxysilane: b.p. 128.0°–128.5° (18 mm), n (20°/D) = 1.4320 (128).

$C_{13}H_{30}Si$ Decyltrimethylsilane: b.p. 151° (200 mm), d (20°/4°) = 0.7705, n (20°/D) = 1.4310 (258).

$C_{13}H_{30}Si$ Heptyltriethylsilane: b.p. 196° (200 mm), d (20°/4°) = 0.7909, n (20°/D) = 1.4422 (258).

$C_{13}H_{30}SiO_3$ Methyltributoxysilane: b.p. 115° (10 mm), n (20°/D) = 1.4106, d (20°/4°) = 0.8775 (132).

$C_{13}H_{30}SiS_4$ Tri-*t*-butylmercaptomethylmercaptosilane: m.p. 43°–44° (307).

$C_{13}H_{30}SiS_4$ *t*-Butylmercaptotri-*i*-propylmercaptosilane: b.p. 160°–162° (3 mm), m.p. 23.0°–23.5° (306).

$C_{14}H_{14}SiCl_2$ Dibenzyldichlorosilane: m.p. 50°–52° (5); b.p. 172°–173° (8 mm) (127).

$C_{14}H_{14}SiCl_2$ Di-*p*-tolyldichlorosilane: b.p. 225°–226° (50 mm) (32).

$C_{14}H_{14}SiO$ Dibenzyloxosilane: m.p. 200° (81).

$C_{14}H_{14}SiO_4Cl_2$ Diguaiacoxydichlorosilane: b.p. 236° (2 mm) (310).

$C_{14}H_{15}SiCl$ Diphenylethylchlorosilane: b.p 206°–208° (760 mm) (4).

$C_{14}H_{15}SiCl$ Dibenzylchlorosilane: b.p. 146°–148° (1 mm) (649).

$C_{14}H_{16}Si$ Dimethyldiphenylsilane: b.p. 176°–178° (45 mm) (35).

$C_{14}H_{16}SiO_2$ Dibenzyldihydroxysilane: m.p. 101° (alpha), 75° (beta) (5); m.p. 101°, 74° (81).

$C_{14}H_{16}SiO_2$ Di-*p*-tolyldihydroxysilane: m.p. 113°–114° (32).

$C_{14}H_{20}SiO_6$ Difurfuroxydiethoxysilane: b.p. 112.5°–123.5° (3 mm) (128).

$C_{14}H_{20}SiO_3$ Phenylethinyltriethoxysilane: b.p. 142° (6 mm), d (22°/22°) = 0.986, n (21°/D) = 1.4898 (224).

$C_{14}H_{23}SiNO$ *m*-Triethylsilicylacetanilide: m.p. 164° (53).

$C_{14}H_{24}Si$ *p*-Ethylphenyltriethylsilane: b.p. 118° (18 mm), d (20°/20°) = 0.8950 (192).

$C_{14}H_{24}SiO$ *p*-α-Hydroxyethylphenyltriethylsilane: b.p. 173°–174° (14.5 mm), d (20°/4°) = 0.9596, n (17.2°/D) = 1.51822 (192).

$C_{14}H_{24}SiO_3$ 2,5-Dimethylphenyltriethoxysilane: b.p. 150° (23 mm) (126).

$C_{14}H_{25}SiO_3N$ *p*-Dimethylaminophenyltriethoxysilane: b.p. 180°–182° (14 mm) (126).

$C_{14}H_{26}SiO_4$ Ethoxytricrotoxysilane: b.p. 133.0°–133.5° (34 mm), n (20°/D) = 1.4320 (129); b.p. 133.0°–133.5° (18 mm), n (20°/D) = 1.4275 (128).

$C_{14}H_{28}Si$ Dicyclohexylethylsilane: b.p. 152° (4 mm) (51).

$C_{14}H_{28}SiO_4$ Dialloxydi-*i*-butoxysilane: b.p. 91 0°–91.5° (3 mm) (128).

$C_{14}H_{28}SiO_4$ Dialloxydi-*t*-butoxysilane: b.p. 61.5°–62.0° (2 mm), n (20°/D) = 1.4121 (128).

$C_{14}H_{28}SiO_8$	Diethyl-α,α'-dicarboxylatodiethyldiethoxysilane: b.p. 155°–160° (14 mm) (303).
$C_{14}H_{29}SiCl_3$	Myristyltrichlorosilane: b.p. 156° (3 mm) (258); b.p. 131°–132° (0.8 mm) (520).
$C_{14}H_{32}Si$	Octyltriethylsilane: b.p. 208° (200 mm), d (20°/4°) = 1.4438 (258).
$C_{14}H_{32}SiOS_3$	Tri-t-butylmercaptoethoxysilane: b.p. 99°–100° (19 mm), n (18°/D) = 1.396 (306).
$C_{14}H_{32}SiO_3$	Ethyltri-i-butoxysilane: b.p. 101°–103° (8 mm) (305).
$C_{14}H_{32}SiO_4$	Ethoxytributoxysilane: b.p. 150.0°–150.5° (32 mm), n (20°/D) = 1.4075 (131).
$C_{14}H_{32}SiS_4$	Tri-t-butylmercaptoethylmercaptosilane: m.p. 26°–27° (307).
$C_{14}H_{32}SiS_4$	Di-t-butylmercaptodi-i-propylmercaptosilane: b.p. 147°–148° (2 mm), m.p. 61.5°–62.5° (306).
$C_{15}H_{18}SiO$	Dibenzylmethylhydroxysilane: b.p. 240°–242° (60 mm) (15).
$C_{15}H_{21}SiO_6Cl$	Tridiacetylmethylchlorosilane: m.p. 96°–98° + dec (545).
$C_{15}H_{21}SiO_6Cl_4Fe$	Tridiacetylmethylchlorosilane ferric chloride: m.p. 187°–188° (139).
$C_{15}H_{25}SiO_3Br$	p-Bromophenyltripropoxysilane: b.p. 175°–176° (14 mm), d (18.8°/4°) = 1.1564, n (16.6°/D) = 1.4850 (192).
$C_{15}H_{25}SiCl$	p-Chlorophenyltripropylsilane: b.p. 160° (14 mm), d (9°/4°) = 0.9708, n (9°/D) = 1.51234 (186, 419).
$C_{15}H_{26}Si$	Dipropylbenzylethylsilane: b.p. 280° (760 mm) (35).
$C_{15}H_{26}Si$	Tri-i-propylphenylsilane: b.p. 90°–91° (4 mm), d (20°/4°) = 0.9055, n (20°/D) = 1.5105 (522).
$C_{15}H_{26}SiO_4$	Cyclohexoxytrialloxysilane: b.p. 104°–105.5° (3 mm) (128).
$C_{15}H_{27}SiO$	p-α-Hydroxypropylphenyltriethylsilane: b.p. 185° (16.5 mm), d (20°/4°) = 0.9575, n (18°/D) = 1.51243 (192).
$C_{15}H_{27}SiO_3Cl$	Alloxydicyclohexoxychlorosilane: b.p. 148°–148.5° (2 mm) (128).
$C_{15}H_{28}SiPb$	p-Trimethylplumbophenyltriethylsilane: b.p. 191° (17 mm), d (23°/4°) = 1.3997, n (23°/D) = 1.54937 (188).
$C_{15}H_{33}SiO_3Cl$	Tri-t-amoxychlorosilane: b.p. 128°–130° (5 mm), d (20°) = 0.924 (587).
$C_{15}H_{33}SiF$	Triamyfluorosilane: b.p. 267° (745 mm), n (25°/D) = 1.4305, d (25°/4°) = 0.8389 (171); b.p. 263°–266° (760 mm), d = 0.8415 (450).
$C_{15}H_{33}SiBr$	Tri-i-amylbromosilane: b.p. 278°–280° (760 mm) (86).
$C_{15}H_{34}Si$	Tri-i-amylsilane: b.p. 275° (760 mm) (86).
$C_{15}H_{34}Si$	Lauryltrimethylsilane: b.p. 222° (200 mm), d (20°/4°) = 0.8036, n (20°/D) = 1.4358 (258).
$C_{15}H_{34}SiO$	Tri-i-amylhydroxysilane: b.p. 269°–270° (760 mm) (86).
$C_{15}H_{34}SiO_4$	Tri-t-butoxy-i-propoxysilane: b.p. 104°–105° (24 mm) (306).
$C_{15}H_{34}SiS_4$	Tri-t-butylmercaptopropylmercaptosilane: m.p. 62.0°–62.5° (306, 307).
$C_{16}H_{12}SiS_4$	Tetra-α-thienylsilane: m.p. 135.5° (202).
$C_{16}H_{18}SiO_2Cl_2$	Diphenyldi-β-chloroethoxysilane: b.p. 142°–146° (0.1 mm), (119, 355); n (20°/D) = 1.5510, d (20°/4°) = 1.2027 (355).
$C_{16}H_{18}SiN_2O_4$	Diethyldi-m-nitrophenylsilane: m.p. 102°–103° (53).
$C_{16}H_{19}SiO_2Br$	p-Bromophenylphenyldiethoxysilane: b.p. 201° (17 mm), d (20°/4°) = 1.2488, n (19°/D) = 1.55031 (192).
$C_{16}H_{19}SiCl$	Dibenzylethylchlorosilane: b.p. 249° (70 mm) (12).

$C_{16}H_{19}SiBr$ p-Bromophenylphenyldiethylsilane: b.p. 203.0°–203.5° (13.5 mm), d (20°/4°) = 1.2153, n (17.9°/D) = 1.5851 (192).

$C_{16}H_{20}Si$ Diethyldiphenylsilane: b.p. 295°–298° (760 mm) (53); b.p. 305°–315° (760 mm) (292).

$C_{16}H_{20}SiO$ Dibenzylethylhydroxysilane: m.p. 54° (5).

$C_{16}H_{20}SiO_2$ Diethyldiphenoxysilane: b.p. 150°–152° (4 mm–5 mm) (127).

$C_{16}H_{20}SiO_2$ Diethoxydiphenylsilane: b.p. 197°–198° (50 mm), b.p. 217°–218° (100 mm), b.p. 302°–304° (760 mm) (37).

$C_{16}H_{20}SiO_8$ Tetramethacryloxysilane: m.p. 73°–75° (364).

$C_{16}H_{21}NO_2S$ Trimethylbenzylsilane p-N-phenylsulfonamide: m.p. 124.2°–125.0° (550).

$C_{16}H_{22}SiN_2$ Diethyldi-m-aminophenylsilane: m.p. 89°–90° (53).

$C_{16}H_{22}SiO_3$ Triethoxy-α-naphthylsilane: b.p. 174°–177° (15 mm–18 mm), b.p. 308°–320° + dec. (744 mm) (411); b.p. 220°–230° (18 mm) (78); b.p. 293°–295° (760 mm) (412).

$C_{16}H_{28}Si$ Benzyl-i-butylethylpropylsilane: b.p. 282°–283° (760 mm) (3, 9).

$C_{16}H_{28}SiO$ p-α-Hydroxy-β-methylpropylphenyltriethylsilane: b.p. 190°–192° (18 mm), d (20°/4°) = 0.9512, n (20°/D) = 1.51212 (192).

$C_{16}H_{28}SiO_4$ Tetracrotonoxysilane: b.p. 148.0°–148.5° (18 mm) (129).

$C_{16}H_{30}SiO_4$ i-Butoxytricrotonoxysilane: b.p. 117.0°–118.0° (3 mm), n (20°/D) = 1.4306 (128).

$C_{16}H_{32}SiO_4$ Di-i-butoxydicrotonoxysilane: b.p. 114.0°–115.0° (3 mm), n (20°/D) = 1.4216 (128).

$C_{16}H_{32}SiO_4$ Di-t-butoxydicrotonoxysilane: b.p. 82°–83° (2 mm), n (20°/D) = 1.4219 (128).

$C_{16}H_{34}SiO_4$ Crotonoxytri-i-butoxysilane: b.p. 106.5°–107.5° (3 mm), n (20°/D) = 1.4135 (128).

$C_{16}H_{36}Si$ Decyltriethylsilane: b.p. 241° (200 mm), d (20°/4°) = 0.8036, n (20°/D) = 1.4472 (258).

$C_{16}H_{36}Si$ Tetrabutylsilane: b.p. 231° (760 mm), d (20°/4°) = 0.822 (349); b.p. 156°–157° (22 mm), d (20°/4°) = 0.8008, 0.8010, d (22°/4°) = 0.8002, n (20°/D) = 1.4465, 1.4463, n (22°/D) = 1.4460 (504).

$C_{16}H_{36}SiO_4$ Tetrabutoxysilane: b.p. 141.0°–142.0° (32 mm), n (20°/D) = 1.4131 (131); b.p. 128°–129° (17 mm), n (18.5°/D) = 1.410 (306); b.p. 273°–277° (760 mm), d (25°/4°) = 0.913 (641).

$C_{16}H_{36}SiO_8$ Tetra-β-ethoxyethoxysilane: b.p. 312° (740 mm), b.p. 200° (9 mm), n (20.5°/D) = 1.4226, d (20°/4°) = 1.0184, d (25°/4°) = 1.0139, viscosity (20°) = 0.0832, (25°) = 0.0334 (641).

$C_{16}H_{36}SiS_4$ Tri-t-butylmercaptobutylmercaptosilane: b.p. 153.5° (760 mm) (306, 307).

$C_{16}H_{35}SiS_4$ Tri-t-butylmercapto-i-butylmercaptosilane: b.p. 146°–148° (1 mm), m.p. 77.0°–77.5° (306, 307).

$C_{16}H_{36}SiS_4$ Tri-t-butylmercapto-s-butylmercaptosilane: m.p. 79°–80° (307).

$C_{16}H_{36}SiS_4$ Tetra-t-butylmercaptosilane: b.p. 160°–161° (306, 307).

$C_{17}H_{23}SiNO_2S$ Benzyltrimethylsilane p-N-benzylsulfonamide: m.p. 130.8°–131.5° (550).

$C_{17}H_{23}SiNO_2S$ Benzyltrimethylsilane p-N-methyl-N-phenylsulfonamide: m.p. 71.5°–72.5° (550).

$C_{17}H_{23}SiNO_2S$ Benzyltrimethylsilane p-N-o-tolylsulfonamide: m.p. 153.0°–153.5° (550).

$C_{17}H_{23}SiNO_2S$ Benzyltrimethylsilane p-N-p-tolylsulfonamide: m.p. 97°–98° (550).

$C_{17}H_{36}SiO_5$ Tri-i-amoxyacetoxysilane: b.p. 124°–127° (1 mm), d (25°/4°) = 0.9252 (583).

$C_{17}H_{36}SiS_4$ Tri-t-butylmercaptocyclopentylmercaptosilane: m.p. 104°–105° (306, 307).

$C_{17}H_{38}Si$ Myristyltrimethylsilane: b.p. 250° (200 mm), d (20°/4°) = 0.7911, n (29°/D) = 1.4410 (258).

$C_{17}H_{38}SiO_3$ Ethyltri-i-amoxysilane: b.p. 151°–154° (17 mm) (305).

$C_{17}H_{38}SiS_4$ Tri-t-butylmercapto-s-amylmercaptosilane: b.p. 169°–170° (2 mm), m.p. 27°–29° (306).

$C_{17}H_{38}SiS_4$ Tri-t-butylmercaptoamylmercaptosilane: m.p. 111.5°–114.0° (306).

$C_{17}H_{38}SiS_4$ Tri-t-butylmercapto-t-amylmercaptosilane: m.p. 111°–114° (307).

$C_{18}H_{12}SiO_3ClBr_3$ Tri-p-bromophenoxychlorosilane: b.p. 310°–320° (12 mm) (83).

$C_{18}H_{15}SiOCl$ Diphenylphenoxychlorosilane: b.p. 252°–254° (40 mm) (37).

$C_{18}H_{15}SiO_2Cl$ Diphenoxyphenylchlorosilane: m.p. 70°–71° (37).

$C_{18}H_{15}SiO_3Cl$ Triphenoxychlorosilane: b.p. 235°–239° (25 mm), b.p. 252°–256° (60 mm) (42); b.p. 229°–239° (13 mm) (83).

$C_{18}H_{15}SiF$ Triphenylfluorosilane: m.p. 64°, b.p. 200°–210° (19 mm) (211); b.p. 101.8° (760 mm), d (17°/4°) = 1.212 (291).

$C_{18}H_{15}SiCl$ Triphenylchlorosilane: m.p. 88°–89° (1, 71); b.p. 378.0° (760 mm) (356).

$C_{18}H_{15}SiBr$ Triphenylbromosilane: m.p. 118°–120° (76).

$C_{18}H_{16}Si$ Triphenylsilane: m.p. 200°–203° (76); b.p. 152°–167° (2 mm), m.p. 36°–37° (203); m.p. 30°–33° (324).

$C_{18}H_{16}SiO$ Triphenylhydroxysilane: m.p. 150° (88); m.p. 148° (1, 368); m.p. 155° (74); m.p. 55°–56° (321).

$C_{18}H_{17}SiN$ Triphenylaminosilane: m.p. 55°–56° (321).

$C_{18}H_{20}SiO_4$ Di-p-hydroxyphenyldiethoxysilane: b.p. 200°–210° (15 mm) (126).

$C_{18}H_{24}Si$ p-Ethylphenylphenyldiethylsilane: b.p. 169°–170° (14 mm), d (20°/4°) = 0.98310, n (20°/D) = 1.56225 (192).

$C_{18}H_{24}Si$ Benzylethylphenylpropylsilane: b.p. 235° (760 mm) (2).

$C_{18}H_{24}SiO_3$ p-Diphenyltriethoxysilane: b.p. 210°–215° (12 mm) (126).

$C_{18}H_{27}SiCl$ Dicyclohexylphenylchlorosilane: b.p. 188°–192° (2 mm), m.p. 45°–48° (50).

$C_{18}H_{27}SiO_9Cl$ Tri-acetylcarboxylatomethylchlorosilane: ethyl ester, m.p. 96°–98° (545).

$C_{18}H_{28}SiO$ Dicyclohexylphenylhydroxysilane: b.p. 145°–146° (50).

$C_{18}H_{31}SiO_3Br$ p-Bromophenyltri-i-butoxysilane: b.p. 190°–191° (14 mm), d (17.2°/4°) = 1.0949, n (14.9°/D) = 1.4787 (192).

$C_{18}H_{32}SiO_3$ Phenyltri-s-butoxysilane: b.p. 154°–157° (10 mm) (305).

$C_{18}H_{32}SiO_4$ Diallyoxydicyclohexoxysilane: b.p. 128.0°–129.0° (3 mm) (128).

$C_{18}H_{34}SiSn$ p-Triethylstanniethylsilane: b.p. 214° (18 mm), d (21.2°) = 1.1216, n (21.0°/D) = 1.5276 (188).

$C_{18}H_{37}SiCl_3$ Octadecyltrichlorosilane: b.p. 159°–162° (13 mm), d (22°/4°) = 0.95.

$C_{18}H_{38}SiS_4$ Tri-t-butylmercaptocyclohexylmercaptosilane: m.p. 64°–65° (306, 307).

$C_{19}H_{18}Si$ Methyltriphenylsilane: m.p. 67.0°–67.5° (4); m.p. 67° (324).

$C_{19}H_{26}Si$	Dibenzylethylpropylsilane: b.p. 262°–264° (10 mm) (12).
$C_{19}H_{40}SiO_4$	Menthoxytripropoxysilane: b.p. 160°–165° (4 mm) (302).
$C_{20}H_{18}SiO_2$	Acetoxytriphenylsilane: m.p. 96°–97° (76); m.p. 91.5° (1); m.p. 91°–92° (368).
$C_{20}H_{20}Si$	Ethyltriphenylsilane: m.p. 72°–74° (76); m.p. 76° (4).
$C_{20}H_{20}SiO_2$	Diphenylethinyldiethoxysilane: b.p. 185° (12 mm), d (9°/9°) = 1.001, n (9°/D) = 1.529 (224).
$C_{20}H_{21}SiN$	Triphenylsilicyl ethyl amine: m.p. 45° (324).
$C_{20}H_{26}SiN_2O_2$	Diethyldi-*m*-acetaminophenylsilane: m.p. 163°–164° (53).
$C_{20}H_{26}SiO_2Cl_2$	Dithymoxydichlorosilane: b.p. 198°–200° (3 mm), d (18°/18°) = 1.1250 (310).
$C_{20}H_{32}Si$	Dicyclohexylethylphenylsilane: b.p. 370° (760 mm) (51).
$C_{20}H_{38}SiO_2Cl_2$	Dimenthoxydichlorosilane: b.p. 193° (8 mm), d (16.5°/4°) = 1.0380, n (16.5°/D) = 1.4709 (299).
$C_{20}H_{44}Si$	Tetraamylsilane: b.p. 305°–312° or 318° (760 mm), d (32°/4°) = 0.8252, n (25°/D) = 1.4510 (85).
$C_{20}H_{44}Si$	Tetra-*i*-amylsilane: b.p. 275° (760 mm) (86).
$C_{20}H_{44}SiO_4$	Tetra-*i*-amoxysilane: d (20°/4°) = 0.8854, n (20°/D) = 1.4183 (355).
$C_{21}H_{21}SiF$	Tribenzylfluorosilane: m.p. 79°, b.p. 235.5° (7.5 mm) (214).
$C_{21}H_{21}SiCl$	Tribenzylcholrosilane: m.p. 141° (5).
$C_{21}H_{21}SiCl$	Tri-*p*-tolylchlorosilane: m.p. 115°–116° (58).
$C_{21}H_{22}Si$	Tribenzylsilane: m.p. 91° (57).
$C_{21}H_{22}SiO$	Tribenzylhydroxysilane: m.p. 106° (75).
$C_{21}H_{22}SiO$	Tri-*p*-tolylhydroxysilane: m.p. 99°–100° (58).
$C_{21}H_{38}SiO_3$	Phenyltri-*i*-amoxysilane: b.p. 194°–197° (18 mm) (305).
$C_{22}H_{24}Si$	Diethylphenylxenylsilane: b.p. 170° (14 mm), d (20°/20°) = 0.931 (192).
$C_{22}H_{32}SiO_2$	Dibenzyldibutoxysilane: b.p. 206°–207° (19 mm) (12).
$C_{24}H_{16}SiN_4O_8$	Tetra-*m*-nitrophenylsilane: m.p. 255°–256° (49).
$C_{24}H_{16}SiBr_4$	Tetra-*p*-bromophenylsilane: b.p. 356° (12 mm) (83).
$C_{24}H_{16}SiSe_4Cl_4$	Tetra-*p*-chlorophenylselenosilane: m.p. 93.5°–94.0° (308).
$C_{24}H_{20}Si$	Tetraphenylsilane: m.p. 228°, b.p. 360° (760 mm) (68); m.p. 227° or 231° (85); m.p. 231°, 232°, 233° (88); m.p. 230°–231° (91, 324); m.p. 234°, d (251.4°/4°) = 0.937, d (263°/4°) = 0.927, d (275°/4°) = 0.917 (409).
$C_{24}H_{20}SiO_2$	Diphenyldiphenoxysilane: m.p. 70°–71° (37, 39).
$C_{24}H_{20}SiO_3$	Phenyltriphenoxysilane: m.p. 40°, b.p. 250° (12 mm) (83).
$C_{24}H_{20}SiO_4$	Tetraphenoxysilane: m.p. 42° (44).
$C_{24}H_{20}SiSe_4$	Tetraphenylselenosilane: m.p. 136.5°–137.0° (308).
$C_{24}H_{24}SiN_4$	Tetra-*m*-aminophenylsilane: m.p. 380° (52).
$C_{24}H_{24}SiN_4$	Tetraanilinosilane: m.p. 137°–138° (317).
$C_{24}H_{29}SiAs$	*p*-Diphenylarsenophenyltriethylsilane: b.p. 279°–281° (17 mm), d (21.3°/4°) = 1.1661, n (21°/D) = 1.61455 (186).
$C_{24}H_{29}SiHgAsCl_2$	*p*-Diphenylaresnophenyltriethylsilane mercuric chloride: m.p. 188° (188).
$C_{24}H_{29}SiHgAsBr_2$	*p*-Diphenylarsenophenyltriethylsilane mercuric bromide: m.p. 181° (188).
$C_{24}H_{29}SiHgAsI_2$	*p*-Diphenylarsenophenyltriethylsilane mercuric iodide: m.p. 139.5° (188).

$C_{24}H_{30}SiGe$	Triethylsilicyltriphenylgermane: m.p. 93.5° (85).
$C_{24}H_{31}SiN_3O$	Tri-p-dimethylaminophenylhydroxysilane: b.p. 275°–280° (12 mm) (126).
$C_{24}H_{38}SiO$	Dicyclohexylcyclohexoxyphenylsilane: m.p. 103°–104° (51).
$C_{25}H_{48}SiO_4$	Cetoxytrialloxysilane: b.p. 225.0°–228.0° (2 mm), n (20°/D) = 1.4440 (128).
$C_{26}H_{24}SiO_2$	Dibenzyldiphenoxysilane: b.p. 230°–231° (1 mm) (127).
$C_{26}H_{58}SiO_4$	Dimenthoxydipropoxysilane: b.p. 223°–230° (5 mm) (303).
$C_{28}H_{28}Si$	Tetra-p-tolylsilane: m.p. 226°, b.p. 360° (760 mm) (68); m.p. 226° (88).
$C_{28}H_{28}Si$	Tetra-m-tolylsilane: m.p. 150.8° (71); m.p. 148° (88).
$C_{28}H_{28}Si$	Tetrabenzylsilane: m.p. 127.5° (68, 214, 215).
$C_{28}H_{28}SiO_8$	Tetra-o-methoxyphenoxysilane: b.p. 317°–323° (12 mm). (83).
$C_{28}H_{28}SiSe_4$	Tetra-p-tolylselenosilane: m.p. 128.0°–128.5° (308).
$C_{28}H_{32}SiN_4$	Tetra-p-methylanilinosilane: m.p. 131°–132° (317).
$C_{30}H_{27}SiO_6Cl$	Tribenzoylacetylmethylchlorosilane: m.p. 188° (295).
$C_{30}H_{27}SiO_6Cl_4Au$	Tribenzoylacetylmethylchlorosilane gold chloride: m.p. 185°–187° or 164° (295).
$C_{30}H_{39}SiO_3Cl$	Trithymoxychlorosilane: b.p. 251°–255° (8 mm), d (20°/20°) = 1.1867 (310).
$C_{30}H_{57}SiO_3Cl$	Trimenthoxychlorosilane: b.p. 244°–245° (10 mm), d (18.5°/4°) = 0.9784, n (18.5°/D) = 1.4699 (299).
$C_{32}H_{32}SiN_4O_4$	Tetra-m-acetaminophenylsilane: m.p. 300°–301° (52).
$C_{32}H_{36}SiO_8$	Tetra-β-phenoxyethoxysilane: m.p. 85°–87° (641).
$C_{36}H_{48}SiN_4$	Tetra-i-propyl-m-aminophenylsilane: m.p. 135° (52).
$C_{36}H_{76}SiO_4$	Dihexadecoxytriethoxysilane: b.p. 312°–316° (15 mm) (303).
$C_{38}H_{78}SiO_5$	Tridodecoxysilicyl acetate: m.p. 5.5°, b.p. 278°–310° (1.5 mm) + dec. (518).
$C_{40}H_{76}SiO_4$	Tetramenthoxysilane: b.p. 264° (7 mm), m.p. 93° (299).
$C_{40}H_{52}SiSe_4$	Tetra-p-t-butylphenylselenosilane: m.p. 175°–176° (308).
$C_{44}H_{86}SiO_8$	Ethyl ricinoleyltriethoxysilane: b.p. 308°–311° (1 mm) (303).
$C_{45}H_{33}SiCl_4Fe$	Tridibenzoylmethylchlorosilane: ferric chloride, m.p. 252°–255° (295).
$C_{45}H_{33}SiCl_4Au$	Tridibenzoylmethylchlorosilane: gold chloride, m.p. 258°–259° (295).
$C_{48}H_{36}Si$	Tetra-p-diphenylsilane: m.p. 270°, 274° (85).
$C_{56}H_{114}SiO_5$	Trioctadecoxysilicyl acetate: m.p. 41.3° (518).
$C_{84}H_{160}SiO_{16}$	Tetra-α-glyceroxysilane tetra-α-stearate: m.p. 70° (306).
$C_{156}H_{296}SiO_{20}$	Tetra-α-glyceroxysilane octa-α,β-stearate: m.p. 68° (301).
H_5Si_2Br	Bromodisilane: m.p. 100°–101° (199).
H_6Si_2	Disilane: m.p. −132°, b.p. −15°, d (−25°) = 0.686 (145, 151).
H_6Si_2O	Disiloxane: m.p. −144°, b.p. −15.2°, d (−80°) = 0.881 (145).
Si_2OCl_6	Hexachlorodisiloxane: b.p. 127° (760 mm), m.p. −35° (88); b.p. 137° (760 mm) (143).
Si_2OBr_6	Hexabromodisiloxane: b.p. 81° (1 mm), m.p. 28° (88); b.p. 81° (1.5 mm) (91).
Si_2Cl_6	Hexachlorodisilane: b.p. 144°–148° (760 mm), m.p. −1° (69); b.p. 90° (125 mm), m.p. 0° (88); b.p. 140°–142° (760 mm) (158); b.p. 145°–146° (760 mm) (166).
Si_2Br_6	Hexabromodisilane: b.p. 240° (760 mm) (69); b.p. 295° (760 mm), m.p. 95° (88, 183).

Si_2I_6	Hexaiododisilane: m.p. $250°$ + dec. (229).
$CH_2Si_2Cl_6$	Hexachlorodisilylmethane: b.p. $63.7°$–$65.0°$ (10 mm) (158, 160).
$CH_3Si_2Cl_5$	Methylpentachlorodisilane: b.p. $51.0°$–$52.5°$ (10 mm) (158, 160).
$CH_3Si_2Cl_5$	Dichlorosilicyltrichlorosilicylmethane: b.p. $52°$ (10 mm) (158).
CH_9Si_2N	N-Methyldisilazine: b.p. $32°$ (760 mm) (312, 313).
$C_2H_4Si_2Cl_6$	1,2-Di-trichlorosilicylethane: m.p. $27°$–$29°$, b.p. $93°$ (25 mm) (158); b.p. $199°$, $202°$ (760 mm) (630).
$C_2H_5Si_2OCl_5$	Ethoxypentachlorodisilane: d ($20°/4°$) = 1.388, n ($14.5°$/D) = 1.4568 (419).
$C_2H_{11}Si_2N$	N-Ethyldisilazine: b.p. $65°$ (760 mm) (312, 313).
$C_3H_6Si_2Cl_6$	1,3-Di-trichlorosilicylpropane: b.p. $111°$ (760 mm) (630).
$C_3H_9Si_2OCl_3$	1,1,1-Trimethyl-3,3,3-trichlorodisiloxane: b.p. $127.0°$–$127.3°$ (754 mm) (524).
$C_4H_{10}Si_2O_2Cl_4$	Diethoxytetrachlorodisilane: d ($20°/4°$) = 1.270, n ($14.5°$/D) = 1.4430 (419).
$C_4H_{12}Si_2OCl_2$	1,1,3,3-Tetramethyl-1,3-dichlorodisiloxane: b.p. $41°$ (20 mm), b.p. $138°$ (760 mm), m.p. $-37.5°$, d ($20°/4°$) = 1.038 (121).
$C_5H_{15}Si_2OCl$	Pentamethylchlorodisiloxane: b.p. $118.6°$–$119.6°$ (758 mm) (524).
$C_6H_{14}Si_2OCl_4$	1,3-Di-dichloromethyl-1,1,3,3-tetramethyldisiloxane: b.p. $150°$ (40 mm), d ($20°/4°$) = 1.2213, n ($20°$/D) = 1.4660 (571).
$C_6Si_2N_6O_7$	Hexa-i-cyanatodisiloxane: b.p. $169°$–$171°$ (14 mm), $260°$ + dec. (760 mm), m.p. $44.5°$ (659).
$C_6Si_2N_6OS_6$	Hexa-i-thiocyanatodisiloxane: b.p. $120°$–$121°$ (760 mm) (659).
$C_6H_{15}Si_2O_3Cl_3$	Triethoxytrichlorodisilane: d ($20°/4°$) = 1.163, n ($14.5°$/D) = 1.4333 (419).
$C_6H_{16}Si_2OCl_2$	1,3-Dichloromethyl-1,1,3,3-tetramethyldisiloxane: b.p. $204.5°$ (760 mm), d ($20°/4°$) = 1.045, n ($20°$/D) = 1.4390 (451).
$C_6H_{17}Si_2OCl$	Pentamethylchloromethyldisiloxane: b.p. $151.6°$–$151.8°$ (760 mm), d ($20°/4°$) = 0.9105, n ($20°$/D) = 1.4106 (451).
$C_6H_{18}Si_2$	Hexamethyldisilane: b.p. $112.5°$–$114.3°$ (755.9 mm), m.p. $12.8°$–$14.0°$, d ($12°/4°$) = 0.7342, d ($17.4°/4°$) = 0.7292, d ($22.5°/4°$) = 0.7247, d ($30.1°/4°$) = 0.7181, d ($50°/4°$) = 0.6983, d ($94.5°/4°$) = 0.6550 (195); b.p. $112.5°$–$114.3°$ (760 mm), d ($24.5°/4°$) = 0.7230 (195).
$C_6H_{18}Si_2O$	Hexamethyldisiloxane: b.p. $100.4°$ (727 mm), n ($20°$/D) = 1.3722, d ($20°/4°$) = 0.7638 (309); b.p. $100°$ (760 mm), n ($20°$/D) = 1.3722 (438); b.p. $99.5°$ (760 mm), m.p. $-69°$, d ($25°/25°$) = 0.7603, n ($25°$/D) = 1.3748 (427); b.p. $100.4°$ (760 mm) (451). 0.7603, n ($25°$/D) = 1.3748 (427); b.p. $100.4°$ (760 mm) (451), b.p. $98°$–$100°$ (760 mm), n ($20°$/D) = 1.3771 (653).
$C_6H_{18}Si_2O_4S$	Di-trimethylsilicyl sulfate: b.p. $87°$–$90°$ (4 mm) (452).
$C_6H_{19}Si_2N$	Hexamethyldisilazine: b.p. $125.7°$–$126.2°$ (758 mm), n ($20°$/D) = 1.4078, d ($20°/4°$) = 0.7741 (311).
$C_7H_{19}Si_2Cl$	Trimethylsilicyldimethylchloromethylsilicylmethane: b.p. $184°$ (732 mm), n ($20°$/D) = 1.4479 (505).
$C_7H_{21}Si_2N$	Heptamethyldisilazine: b.p. $143°$–$144°$ (311).
$C_8H_{20}Si_2O_4$	Dimeric dimethylethylenedioxysilane: m.p. $55°$, d ($20°/4°$) = 1.0585, n ($20°$/D) = 1.4380 (631).
$C_8H_{20}Si_2O_4$	Tetramethyl-1,3-(2,2'-oxydiethoxy)-disiloxane: b.p. $100°$ (50 mm), d ($20°/4°$) = 1.0452, n ($20°$/D) = 1.4275 (631).

$C_8H_{22}Si_2O$ Trimethylsilicylmethyldimethylethoxysilane: b.p. 160° (740 mm), n (25°/D) = 1.4148, d (25°) = 0.8060 (575).

$C_8H_{22}Si_2O_3$ 1,3-Diethoxy-1,1,3,3-tetramethyltrisiloxane: b.p. 160° (743 mm), b.p. 161° (760 mm), b.p. 64.5° (20 mm), d (20°) = 0.879, n (20°/D) = 1.3880 (617); b.p. 158° (760 mm), d (20°/4°) = 0.8831, n (20°/D) = 1.3880 (631).

$C_9H_{24}Si_2O$ 1,1,1-Trimethyl-3,3,3-triethyldisiloxane: b.p. 172° (724 mm), 80° (30 mm), n (20°/D) = 1.4104, 1.4105 (650).

$C_{10}H_{25}Si_2O_5Cl$ Pentaethoxychlorodisilane: d (17°/4°) = 1.092, n (14.5°/D) = 1.4205 (419).

$C_{12}H_{19}Si_2Cl_3$ p-Trichlorosilicylphenyltriethylsilane: b.p. 173°–176° (16.5 mm) (192).

$C_{12}H_{30}Si_2$ Hexaethyldisilane: b.p. 250° (760 mm) (88); b.p. 250°–253° (760 mm) (69); b.p. 255° (760 mm), d (0°) = 0.8510, d (20°) = 0.8403 (413); b.p. 250°–253° (750 mm) (557).

$C_{12}H_{30}Si_2O$ Hexaethyldisiloxane: b.p. 231° (760 mm), d (0°) = 0.8590 (66); b.p. 233° (758 mm) (361), b.p. 129° (30 mm), n (20°/D) = 1.4340, 1.4332 (650).

$C_{12}H_{30}Si_2O$ 1,1,3,3-Tetra-i-propyldisiloxane: b.p. 129°–130° (6 mm), d (20°/4°) = 0.8899, n (20°/D) = 1.4692 (522).

$C_{12}H_{30}Si_2O_3$ 1,1,3,3-Tetramethyl-1,3-dibutoxydisiloxane: b.p. 224.5°–225.5° (741 mm), 99°–100° (10 mm), n (20°/D) = 1.4051, d (20°/4°) = 0.8733 (132).

$C_{12}H_{30}Si_2O_4S$ Di-triethylsilicyl sulfate: b.p. 128° (2 mm) (438); b.p. 170° (12 mm), n (20°/D) = 1.4442 (438, 452).

$C_{12}H_{30}Si_2O_6$ Hexaethoxydisilane: d (17°/4°) = 0.9718, n (14.5°/D) = 1.4134 (419); b.p. 132°–133° (18 mm) (641).

$C_{12}H_{30}Si_2O_7$ Hexaethoxydisiloxane: b.p. 235°–237° (64); b.p. 235° (760 mm) (143); b.p. 95.5°–96.5° (3 mm) (128); b.p. 233 (743 mm), n (20°/D) = 1.4340 (363); b.p. 160° (18 mm) (642).

$C_{14}H_{30}Si_2O_7$ 1,1,3,3-Tetraethoxy-1,3-diallyloxydisiloxane: b.p. 149°–151° (18 mm), n (20°/D) = 1.4080 (128).

$C_{16}H_{22}Si_2O_2$ 1,2-Diethyl-1,2-diphenyl-1,2-dihydroxydisilane: b.p. 244°–248° (20 mm) (27).

$C_{16}H_{22}Si_2O_3$ 1,3-Diethyl-1,3-diphenyl-1,3-dihydroxydisiloxane: m.p. 87.5° (20, 349).

$C_{18}H_{34}Si_2$ p-Ditriethylsilicylbenzene: b.p. 195°–196° (16.5 mm), d (20°/4°) = 0.8967, n (20°/D) = 1.50942 (192).

$C_{18}H_{42}Si_2$ Hexapropyldisilane: b.p. 114° (3 mm), n (20°/D) = 1.4740, d (26°/4°) = 0.8693 (88).

$C_{18}H_{42}Si_2O$ Hexapropyldisiloxane: b.p. 285° (760 mm) (349); b.p. 206°–209° (347).

$C_{18}H_{42}Si_2O_6$ Hexapropoxydisilane: b.p. 190°–195° (25 mm) (641).

$C_{18}H_{42}Si_2O_7$ Hexaproproxydisiloxane: b.p. 350° + dec. (760 mm), b.p. 195° (20 mm) (443); b.p. 205°–208° (25 mm), d (20°/4°) = 0.977 (641).

$C_{20}H_{30}Si_2O$ 1,1,3,3-Tetraethyl-1,3-diphenyldisiloxane: b.p. 258° (75 mm) (18 mm).

$C_{20}H_{34}Si_2O_8$ 1,2-Di-triallyloxysiloxyethane: n (20°/D) = 1.4487 (128).

$C_{22}H_{34}Si_2O_6S_2$ 1,2-Diethyl-1,2-diphenyl-1,2-dipropyldisilane: p,p'-disulfonic acid, m.p. 220° (27).

$C_{22}H_{38}Si_2O_9$	1,5-Di-trialloxysiloxydiglycol: n (20°/D) = 1.4510 (128).
$C_{24}H_{20}Si_2OCl_2$	1,1,3,3-Tetraphenyl-1,3-dichlorodisiloxane: m.p. 38°, b.p. 238°–241° (1 mm) (329).
$C_{24}H_{22}SiO_3$	1,1,3,3-Tetraphenyl-1,3-dihydroxydisiloxane: m.p. 113° (349), m.p. 113°–114° (18, 349).
$C_{24}H_{38}Si_2$	Benzylethylpropyldisilane: b.p. 244° (20 mm) (349).
$C_{24}H_{38}Si_2O$	Benzylethylpropyldisiloxane: b.p. 272° (50 mm) (349).
$C_{24}H_{42}Si_2O_7$	Hexacrotoxydisiloxane: b.p. 176.0°–178.0° (4 mm), n (20°/D) = 1.4414 (128).
$C_{24}H_{54}Si_2O_7$	Hexabutoxydisiloxane: b.p. 245°–250° (20 mm) (641).
$C_{24}H_{54}Si_2O_7$	Hexa-*t*-butoxydisiloxane: m.p. 260° + dec. (306).
$C_{26}H_{26}Si_2O$	1,3-Dimethyl-1,1,3,3-tetraphenyldisiloxane: m.p. 51°–52° (35).
$C_{26}H_{42}Si_2O$	1,3-Dibenzyl-1,3-di-*i*-butyl-1,3-diethyldisiloxane: b.p. 250°–252° (25 mm) (7).
$C_{26}H_{46}Si_2O_8$	1,2-Di-trimethalloxysiloxyethane: n (20°/D) = 1.4487 (128).
$C_{28}H_{28}Si_2O_3Br_2$	1,3-Diphenyl-1,3-di-*p*-bromophenyl-1,3-diethoxydisiloxane: b.p. 317°–318° (20 mm), d (20°/4°) = 1.3639, n (17.6°/D) = 1.58434 (192).
$C_{28}H_{30}Si_2O$	1,1,3,3-Tetraphenyl-1,3-diethyldisiloxane: m.p. 65.4° (4).
$C_{28}H_{30}Si_2O_3$	1,1,3,3-Tetrabenzyl-1,3-dihydroxydisiloxane: m.p. 76° (349).
$C_{30}H_{34}Si_2O$	1,1,3,3-Tetrabenzyl-1,3-dimethyldisiloxane: m.p. 56° (15).
$C_{28}H_{58}Si_2O_9$	1,5-Di-trimethalloxysiloxydiglycol: n (20°/D) = 1.4510 (128).
$C_{30}H_{66}Si_2O$	Hexa-*i*-amyldisiloxane: b.p. 360°–370° (86).
$C_{32}H_{38}Si_2O$	1,3-Diethyl-1,1,3,3-tetrabenzyldisiloxane: m.p. 54° (5).
$C_{36}H_{30}Si_2$	Hexaphenyldisilane: m.p. 354° (8); m.p. 341°, 342°, 345° (88); m.p. 352° (91); m.p. 360° (13); m.p. 351°–353° (324).
$C_{36}H_{30}Si_2O$	Hexaphenyldisiloxane: m.p. 222° (1, 74); m.p. 210°, 220° (88); m.p. 220° (91); m.p. 221° (368).
$C_{36}H_{31}Si_2N$	Di-triphenylsilicyl amine: m.p. 175° (203).
$C_{42}H_{42}Si_2$	Hexabenzyldisilane: m.p. 194° (91).
$C_{42}H_{42}Si_2$	Hexa-*p*-tolyldisilane: m.p. 345° (88).
$C_{42}H_{42}Si_2O$	Hexabenzyldisiloxane: m.p. 205° (57).
$C_{42}H_{42}Si_2O$	Hexa-*p*-tolyldisiloxane: m.p. 223°–224° (58).
H_8Si_3	Trisilane: m.p. −117°, d (0°) = 0.725 (151).
Si_3Br_8	Octabromotrisilane: m.p. 133° (183).
Si_3Cl_8	Octachlorotrisilane: b.p. 210° (760 mm) (73); b.p. 210°–215° (760 mm) (166); b.p. 215°–218° (760 mm), m.p. −67° (168).
H_9Si_3N	Trisilicyl amine: b.p. 52° (200).
$Si_3O_2Cl_8$	Octachlorotrisiloxane: b.p. 76° (15 mm) (143).
$C_3H_6Si_3Cl_6$	Cyclotri-methylenedichlorosilane: m.p. 81.0°–82.5° (158, 160).
$C_6H_{18}Si_3O_3$	Hexamethylcyclotrisiloxane: b.p. 134° (760 mm), m.p. 64° (262); b.p. 135° (760 mm) (122); b.p. 133° (760 mm), m.p. 64.5° (133).
$C_6H_{18}Si_3O_2Cl_2$	1,1,3,3,5,5-Hexamethyl-1,5-dichlorotrisiloxane: m.p. −53°, b.p. 79° (20 mm), b.p. 184° (760 mm), d (20°/4°) = 1.018 (121).
$C_7H_{22}Si_3O_2$	1,1,1,3,5,5,5-Heptamethyltrisiloxane: d (20°/4°) = 0.8194, n (20°/D) = 1.3818 (266).
$C_8H_{24}Si_3O_2$	Octamethyltrisiloxane: b.p. 152° (760 mm), m.p. −86°, d (25°/25°) = 0.8122, n (25°/D) = 1.3822 (427).
$C_8Si_3N_8O_{10}$	Octa-*i*-cyanatotrisiloxane: b.p. 170° (2 mm) (659).

$C_9H_{27}Si_3PO_4$ Tri-trimethylsilicyl phosphate: b.p. 170° (12 mm), n (20°/D) = 1.4442 (215); b.p. 85°–87° (4 mm), n (20°/D) = 1.4090 (309).

$C_{10}H_{28}Si_3$ Octamethyltrisilicylmethylene: b.p. 202° (760 mm), n (20°/D) = 1.4414, d (20°/4°) = 0.8002 (505).

$C_{10}H_{28}Si_3O_4$ 1,5-Diethoxy-1,1,3,3,5,5-hexamethyltrisiloxane: b.p. 95° (20 mm), 133° (100 mm), 196° (760 mm), d (20°) = 0.902, n (20°/D) = 1.3922 (617).

$C_{12}H_{30}Si_3O_3$ Hexaethylcyclotrisiloxane: b.p. 140°–148° (17 mm) (96).

$C_{14}H_{36}Si_3O_4$ 1,1,3,3,5,5-Hexamethyl-1,5-dibutoxytrisiloxane: b.p. 124°–125° (10 mm), n (20°/D) = 1.4053, d (20°/4°) = 0.8932 (132).

$C_{16}H_{40}Si_3O_{10}$ Octaethoxytrisiloxane: b.p. 268°–273° (760 mm) (143).

$C_{24}H_{30}Si_3O_3$ sym-triethyltriphenylcyclotrisiloxane: m.p. 177.5° (96).

$C_{24}H_{54}Si_3O_9$ Hexabutoxycyclotrisiloxane: b.p. 185°–190° (760 mm), n (20°) = 1.4186 (591).

$C_{27}H_{36}Si_3O_3$ sym-Tribenzyltriethylcyclotrisiloxane: b.p. 310° (22 mm) (349).

$C_{28}H_{30}Si_3O_4$ 1,3,3,5-Tetrabenzyl-1,5-dihydroxytrisiloxane: m.p. 82° (349).

$C_{36}H_{30}Si_3O_3$ Hexaphenylcyclotrisiloxane: m.p. 199.5°–200.5° (96); m.p. 188°–189° (188); m.p. 190°, b.p. 290°–300° (1 mm), 298°–310° (1 mm) (329).

$C_{36}H_{30}Si_3O_2Cl_2$ 1,1,3,3,5,5-Hexaphenyl-1,5-dichlorotrisiloxane: b.p. 290°–293° (1 mm) (329).

$C_{36}H_{32}Si_3O_4$ 1,1,3,3,5,5-Hexaphenyl-1,5-dihydroxytrisiloxane: m.p. 111°–112° (18); m.p. 111° (329).

$C_{36}H_{48}Si_3O_3$ sym-Tricyclohexyltriphenylcyclotrisiloxane: m.p. 117°–118° (50).

$C_{36}H_{66}Si_3O_3$ Hexacyclohexylcyclotrisiloxane: m.p. 237°–239° (50).

$C_{42}H_{42}Si_3O_3$ Hexabenzyltrisiloxane: m.p. 98° (5, 34).

$C_{42}H_{42}Si_3O_2$ Hexa-p-tolylcyclotrisiloxane: m.p. 223°–224° (58).

$C_{42}H_{44}Si_3O_4$ 1,1,3,3,5,5-Hexabenzyl-1,5-dihydroxytrisiloxane: m.p. 117°–118° (22).

$H_{10}Si_4$ Tetrasilane: m.p. −93.5°, d (0°) = 0.79 (151).

$Si_4O_3Cl_{10}$ Decachlorotetrosiloxane: b.p. 109°–110° (15 mm) (143).

$Si_4O_4Cl_8$ Octachlorocyclotetrasiloxane: b.p. 91° (15 mm) (143).

$C_4H_{16}Si_4O_4$ 2,4,6,8-Tetramethylcyclotetrasiloxane: b.p. 134.5°–135.0° (755 mm), m.p. −69°, n (20°/D) = 1.3870: d (20°/4°) = 0.9912 (267).

$C_8H_{23}Si_4O_4Cl$ Hexamethylcyclotrisiloxane-methylchloromethyloxosilane: m.p. −1°, b.p. 214°, d (20°/20°) = 1.044, n (20°/D) = 1.4158 (571).

$C_8H_{24}Si_4O_3Cl_2$ 1,1,3,3,5,5,7,7-Octamethyl-1,7-dichlorotetrasiloxane: m.p. −62°, b.p. 111° (20 mm), b.p. 222° (760 mm), d (20°/4°) = 1.011 (121).

$C_8H_{24}Si_4O_4$ Octamethylcyclotetrasiloxane: b.p. 70° (24 mm), b.p. 175° (760 mm), d (20°/4°) = 0.9558, n (20°/D) = 1.3968 (262); b.p. 170° (760 mm) (122); b.p. 73° (20 mm) (617); b.p. 171° (760 mm), m.p. 17.4°, d (25°) = 0.9497, n (25°/D) = 1.3935 (133).

$C_8H_{26}Si_4O_3$ 1,1,1,3,5,7,7,7-Octamethyltetrasiloxane: d (20°/4°) = 0.8559 n (20°/D) = 1.3854 (266).

$C_9H_{28}Si_4O_3$ 1,1,1,5,5,5-Hexamethyl-3-trimethylsiloxytrisiloxane: b.p. 183.6°–190.6° (760 mm), d (20°/4°) = 0.8553, n (20°/D) = 1.3872 (266).

$C_{10}H_{30}Si_4O_2$ Decamethyltetrasiloxane: b.p. 153° (760 mm), m.p. −80°, d (20°/4°) = 0.8200, n (20°/D) = 1.3843 (262).

$C_{10}H_{30}Si_4O_3$ 1,1,1,3,5,5,5-Heptamethyl-3-trimethylsiloxytrisiloxane: m.p. −80°, d (20°/4°) = 0.8497, n (20°/D) = 1.3880 (262).

$C_{12}H_{64}Si_4O_5$	1,7-Diethoxy-1,1,3,3,5,5,7,7-octamethyltetrasiloxane: b.p. 55° (0.4–0.5 mm), 123° (20 mm), 160° (91 mm), 227° (760 mm), d (20°) = 0.916, n (20°/D) = 1.3950 (617).
$C_{16}H_{40}Si_4O_{12}$	Octaethoxycyclotetrasiloxane: d (0°) = 1.071, d (14.5°) = 1.054 (359).
$C_{20}H_{50}Si_4O_{13}$	Decaethoxytetrasiloxane: b.p. 290°–295° (760 mm) (143).
$C_{32}H_{72}Si_4O_{12}$	Octabutoxycyclotetrasiloxane: b.p. 220°–225° (760 mm), n (20°) = 1.4220 (591).
$C_{48}H_{40}Si_4O$	Octaphenyltetrasilane oxide: m.p. 210°–245° (28).
$C_{48}H_{40}Si_4O_2$	Octaphenyltetrasilane dioxide: (cyclic) m.p. 222° (349).
$C_{48}H_{40}Si_4O_4$	Octaphenylcyclotetrasiloxane: m.p. 200°–201° (18, 349).
$C_{48}H_{42}Si_4O_5$	Octaphenyl-1,7-dihydroxytetrasiloxane: m.p. 128.5° (23).
$C_{52}H_{56}Si_4O_3$	Diethyloctaphenyltetrasilane trihydrate: m.p. 253°–254° (31).
$C_{56}H_{54}Si_4$	Octa-p-tolylcyclotetrasilane: m.p. 310° (44).
$C_{56}H_{56}Si_4$	Octa-p-tolyltetrasilylene-1,4: m.p. 290°–293° (44).
$C_{56}H_{56}Si_4O$	Octa-p-tolyltetrasilane oxide: m.p. 228°–229° (44).
$C_{56}H_{56}Si_4O_4$	Octa-p-tolylcyclotetrasiloxane: m.p. 186°–187° (32).
$C_{56}H_{56}Si_4I_2$	1,1,2,2,3,3,4,4-Octa-p-tolyl-1,4-diiodotetrasilane: m.p. 300° (44).
$C_{60}H_{50}Si_4O_2$	Diphenoxyoctaphenyltetrasilane: m.p. 215°–216° (37); m.p. 216° (349).
$Si_5O_4Cl_{12}$	Dodecachloropentasiloxane: b.p. 130°–131° (15 mm) (143).
Si_5Cl_{12}	Dodecachloropentasilane: b.p. 150° (15 mm) (168).
$C_5H_{20}Si_5O_5$	2,4,6,8,10-Pentamethylcyclopentasiloxane: b.p. 168.8°–168.9° (755 mm), m.p. −108°, d (20°/4°) = 0.9985, n (20°/D) = 1.3912 (266).
$C_9H_{30}Si_5O_4$	1,1,1,3,5,7,9,9,9-Nonamethylpentasiloxane: b.p. 85.6° (10 mm), d(20°/4°) = 0.8806, n (20°/D) = 1.3878 (266).
$C_{10}H_{30}Si_5O_4Cl_2$	1,1,3,3,5,5,7,7,9,9-Decamethyl-1,9-dichloropentasiloxane: m.p. −80°, b.p. 138° (20 mm), d (20°/4°) = 1.005 (121).
$C_{10}H_{30}Si_5O_5$	Decamethylcyclopentasiloxane: b.p. 50°–75° (4 mm) (122); 101° (20 mm), m.p. −38°, m.p. 210° (760 mm), d (20°/4°) = 0.9593, n (20°/D) = 1.3982 (262); b.p. 100° (20 mm) (617); b.p. 204.5° (760 mm), m.p. −44°, d (25°) = 0.9531, n (28°/D) = 1.3958 (133).
$C_{12}H_{36}Si_5O_4$	Dodecamethylpentasiloxane: b.p. 194° (760 mm), m.p. −70°, d (20°/4°) = 0.8536, n (20°/D) = 1.3895 (262); m.p. −84°, d (25°/25°) = 0.8710, n (25°/D) = 1.3902 (427).
$C_8H_{24}Si_5O_6$	Octamethylpolycyclopolysiloxane: m.p. 118°, b.p. 203° (263).
$C_8H_{24}Si_5O_6$	Octamethylspiropolysiloxane: m.p. 121°, b.p. 204° (263).
$C_{14}H_{40}Si_5O_6$	1,9-Diethoxy-1,1,3,3,5,5,7,7,9,9-decamethylpentasiloxane: b.p. 72° (0.4–0.5 mm), 146° (20 mm), 253 (760 mm), d (20°) = 0.920, n (20°/D) = 1.3965 (617).
$C_{24}H_{60}Si_5O_{16}$	"Ethyl Silicate 40": d (20°/20°) = 1.050–1.070 (586).
$C_{40}H_{90}Si_5O_{15}$	Decabutoxycyclopentasiloxane: b.p. 245°–250° (760 mm) n (20°) = 1.4228 (591).
$Si_6O_5Cl_{14}$	Quadradecachlorohexasiloxane: b.p. 139°–141° (15 mm) (143).
Si_6Cl_{14}	Quadradecachlorohexasilane: sub. p. 200° + dec. (168).
$C_6H_{24}Si_6O_6$	2,4,6,8,10,12-Hexamethylcyclohexasiloxane: b.p. 92.6°–93.0° (2 mm), m.p. −79°, d (20°/4°) = 1.006, n (20°/D) = 1.3944 (266).
$C_8H_{24}Si_6O_8$	Octamethylpolycyclopolysiloxane: m.p. 119°, b.p. 220° (263).

$C_{10}H_{30}Si_6O_5$ 1,1,1,3,5,7,9,11,11,11-Decamethylhexasiloxane: b.p. 106.5°–107.6° (10 mm), d (20°/4°) = 0.8991, n (20°/D) = 1.3895 (266).

$C_{10}H_{30}Si_6O_7$ Decamethylpolycyclosiloxane: m.p. 51°, b.p. 232° (263).

$C_{10}H_{30}Si_6O_7$ Decamethylspiropolysiloxane: m.p. 57° b.p. 230° (263).

$C_{12}H_{36}Si_6O_8Cl_2$ 1,1,3,3,5,5,7,7,9,9,11,11 - Dodecamethyl - 1,11-dichlorohexasiloxane: m.p. less than −80°, b.p. 161° (20 mm), d (20°/4°) = 1.003 (121).

$C_{12}H_{36}Si_6O_6$ Dodecamethylcyclohexasiloxane: b.p. 75°–100° (4 mm) (122); b.p. 128° (20 mm), m.p. −3°, b.p. 245° (760 mm), d (20°/4°) = 0.9672, n (20° D) = 1.4015 (262); b.p. 236° (760 mm), m.p. −3; d (25°) = 0.9613, n (25°/D) = 1.3996 (133).

$C_{14}H_{42}Si_6O_5$ Quadradecamethylhexasiloxane: b.p. 229° (760 mm), m.p. −80°, d 20°/4) = 0.8755, n (20°/D) = 1.3925 (262); m.p. −59°, d (25°/25°) = 0.8873, n (25°/D) = 1.3922 (427).

$C_{16}H_{46}Si_6O_7$ 1,11-Diethoxy-1,1,3,3,5,5,7,7,9,9,11,11-dodecamethylhexasiloxane: b.p. 91° (0.4 mm–0.5 mm), 274° (760 mm), d (20°) = 0.932, n (20°/D) = 1.3980 (617).

$C_{28}H_{70}Si_6O_{19}$ Quadradecaethoxyhexasiloxane: b.p. 300°–310° (760 mm) (143).

$C_{48}H_{108}Si_6O_{18}$ Dodecabutoxycyclohexasiloxane: b.p. 275°–280° (760 mm), n (20°) = 1.4230 (591).

$Si_7O_6Cl_{16}$ Hexadecachloroheptasiloxane: b.p. 145°–147° (15 mm) (143).

$C_{10}H_{30}Si_7O_9$ Decamethylpolycyclosiloxane: m.p. 150°, b.p. 248° (760 mm) (263).

$C_{12}H_{36}Si_7O_8$ Polymeric silicone: b.p. 254° (760 mm), m.p. 31°, d (20°/4°) = 1.0352, n (20°/D) = 1.4031 (263).

$C_{12}H_{36}Si_7O_8$ Dodecamethylspiropolysiloxane: m.p. 31°, b.p. 254° (760 mm) (263).

$C_{14}H_{42}Si_7O_7$ Quadradecamethylcycloheptasiloxane: b.p. 154° (20 mm), m.p. −26°, d (20°/4°) = 0.9730, n (20°/D) = 1.4040 (262); b.p. 100°–125° (4 mm) (122); b.p. 147° (20 mm), b.p. −32; d (25°) = 0.9664, n (25°/D) = 1.4018 (133).

$C_{16}H_{48}Si_7O_6$ Hexadecamethylheptasiloxane: b.p. 142° (20 mm), m.p. below −100°, d (20°/4°) = 0.8910, n (20°/D) = 1.3940 (262); m.p. −78°, d (25°/25°) = 0.9004, n (25°/D) = 1.3940 (427).

$C_{18}H_{52}Si_7O_8$ 1,13-Diethoxyquadradecamethylheptasiloxane: b.p. 107° (0.4–0.5 mm), b.p. 295° (760 mm), d 20°) = 0.936, n (20°/D) = 1.3990 (617).

$C_{10}H_{30}Si_8O_{11}$ Decamethylpolycyclopolysiloxane: m.p. 139°, b.p. 257° (760 mm) (263).

$C_{14}H_{42}Si_8O_9$ Polymerized silicone: b.p. 157° (20 mm), m.p. −12°, d (20°/4°) = 1.0260, n (20°/D) = 1.4023 (263).

$C_{14}H_{42}Si_8O_9$ Quadradecamethylspiropolysiloxane: m.p. 212°, b.p. 157° (20 mm) (263).

$C_{16}H_{48}Si_8O_8$ Hexadecamethylcyclooctasiloxane: b.p. 125°–150° (4 mm), (122); b.p. 175° (20 mm), m.p. 30°, n (20°/D) = 1.4060 (262); b.p. 168° (20 mm); m.p. 31.5; n (25°/D) = 1.4039 (133).

$C_{18}H_{54}Si_8O_7$ Octadecamethyloctasiloxane: m.p. −63°, d;(25°/25°) = 0.9078, n (25°/D) = 1.3952 (427).

$C_{20}H_{58}Si_8O_9$ 1,15-Diethoxyhexadecamethyloctasiloxane: b.p. 121° (0.5 mm), b.p. 315° (760 mm), d (20°) = 0.941, n (20°/D) = 1.3997 (617).

$C_{64}H_{144}Si_8O_{24}$ Hexadecabutoxycyclooctasiloxane: b.p. 300°–326° (760 mm), n (20°/D) = 1.4240 (591).

$C_{18}H_{54}Si_9O_9$ Octadecamethylcyclononasiloxane: b.p. 188° (20 mm), n (20°/D) = 1.4040 (262).

$C_{22}H_{64}Si_9O_{10}$ 1,17-Diethoxyoctadecamethylnonasiloxane: b.p. 131° (0.2 mm–0.4 mm), d (20°/4°) = 0.944, n (20°/D) = 1.4002 (617).

$Si_{10}Cl_{22}$ Duovigesimochlorodecasilane: b.p. 215°–220° (760 mm) (208).

$C_{22}H_{66}Si_{10}O_9$ Duovigesimomethoxyldecasilane: b.p. 203° (10 mm), d = 0.925, n = 1.3988 (346).

$C_{24}H_{70}Si_{10}O_{11}$ 1,19-Diethoxyvigesimomethyldecasiloxane: b.p. 147° (0.2 mm–0.4 mm), d (20°) = 0.947, n (20°/D) = 1.4009 (617).

$C_{24}H_{72}Si_{11}O_{10}$ Quadravigesimomethylundecasiloxane: b.p. 202° (4.7 mm), d = 0.930, n = 1.3994 (346).

$C_{26}H_{76}Si_{11}O_{12}$ 1,21-Diethoxyduovigesimomethylundecasiloxane: b.p. 157°–158° (0.2 mm–0.4 mm), d (20°) = 0.950, n (20°/D) = 1.4012 (617).

Bibliography

1. F. S. Kipping, *J. Chem. Soc.*, **79**, 449 (1901).
2. —, *ibid.*, **91**, 209 (1907).
3. —. *ibid.*, **91**, 717 (1907).
4. —, *ibid.*, **93**, 198 (1908).
5. —, *ibid.*, **93**, 439 (1908).
6. —, *ibid.*, **93**, 457 (1908).
7. —, *ibid.*, **93**, 2004 (1908).
8. —, *ibid.*, **93**, 2090 (1908).
9. —, *ibid.*, **95**, 69 (1909).
10. G. Martin and F. S. Kipping, *ibid.*, **95**, 302 (1909).
11. F. S. Kipping and G. Martin, *ibid.*, **95**, 489 (1909).
12. F. Challenger and F. S. Kipping, *ibid.*, **97**, 142 (1910).
13. F. S. Kipping, *Proc. Roy. Soc.*, **27**, 143 (1911).
14. F. Challenger and F. S. Kipping, *J. Chem. Soc.*, **97**, 755 (1910).
15. F. S. Kipping and F. M. Hackford, *ibid.*, **99**, 138 (1911).
16. —, *ibid.*, **101**, 2106 (1912).
17. —, *ibid.*, **101**, 2108 (1912).
18. —, *ibid.*, **101**, 2125 (1912).
19. R. Robison and F. S. Kipping, *ibid.*, **101**, 2142 (1912).
20. —, —, *ibid.*, **101**, 2156 (1912).
21. T. A. Smith and F. S. Kipping, *ibid.*, **101**, 2553 (1912).
22. R. Robison and F. S. Kipping, *ibid.*, **105**, 40 (1914).
23. F. S. Kipping and R. Robison, *ibid.*, **105**, 484 (1914).
24. J. A. Meads and F. S. Kipping, *ibid.*, **107**, 679 (1915).
25. F. S. Kipping, *Chem. News*, **111**, 135 (1915).
26. J. A. Meads and F. S. Kipping, *J. Chem. Soc.*, **107**, 459 (1915).
27. F. S. Kipping, *ibid.*, **119**, 647 (1921).
28. —, and J. E. Sands, *ibid.*, **119**, 830 (1921).
29. —, —, *ibid.*, **119**, 848 (1921).
30. —, *ibid.*, **123**, 2590 (1923).
31. —, *ibid.*, **123**, 2598 (1923).
32. H. S. Pink and F. S. Kipping, *ibid.*, **123**, 2830 (1923).
33. F. S. Kipping, *ibid.*, **125**, 2291 (1924).
34. L. R. Vyle and F. S. Kipping, *ibid.*, **125**, 2616 (1924).
35. F. S. Kipping, *ibid.*, 104 (1927).
36. —, *ibid.*, 2719 (1927).
37. —, *ibid.*, 2728 (1927).
38. —, and A. G. Murray, *ibid.*, 2734 (1927).
39. —, —, *ibid.*, 1427 (1928).
40. —, —, *ibid.*, 1431 (1928).
41. —, —, *ibid.*, 360 (1928).
42. R. A. Thompson and F. S. Kipping, *ibid.*, 1176 (1929).
43. F. S. Kipping, A. G. Murray and J. G. Maltby, *ibid.*, 1180 (1929

44. A. R. Steele and F. S. Kipping, *ibid.*, 2545 (1929).
45. K. W. Palmer and F. S. Kipping, *ibid.*, 1020 (1930).
46. F. S. Kipping and J. F. Short, *ibid.*, 1029 (1930).
47. —, J. C. Blackburn and J. F. Short, *ibid.*, 1290 (1931).
48. W. E. Evison and F. S. Kipping, *ibid.*, 2774 (1931).
49. F. S. Kipping and J. C. Blackburn, *ibid.*, 2200 (1932).
50. N. W. Cusa and F. S. Kipping, *ibid.*, 2206 (1932).
51. —, —, *ibid.*, 1040 (1933).
52. —, and J. C. Blackburn, *J. Chem. Soc.*, 1083 (1935).
53. —, and N. W. Cusa, *ibid.*, 1088 (1935).
54. —, and J. T. Abrams, *ibid.*, 81 (1944).
55. —, and R. A. Thompson, *ibid.*, 1137 (1928).
56. —, —, *ibid.*, 1989 (1928).
57. W. E. Evison and F. S. Kipping, *J. Chem. Soc.*, 2830 (1931).
58. A. R. Steele and F. S. Kipping, *ibid.*, 357 (1939).
59. C. Friedel and J. Crafts, *Ann.* **127**, 28 (1863).
60. —, —, *Ann.*, **136**, 203 (1865).
61. —, —, *Ann.*, **138**, 19 (1865).
62. —, and A. Ladenburg, *Ann.*, **143**, 118 (1867).
63. —, —, *Ann.*, **145**, 179 (1868).
64. —, —, *Ann.*, **147**, 355 (1868).
65. —, —, *Ber.*, **3**, 15 (1870).
66. A. Ladenburg, *Ann.*, **164**, 309 (1872).
67. —, *Ann.*, **173**, 143 (1874).
68. A. Polis, *Ber.*, **18**, 1542 (1885).
69. C. Friedel and A. Ladenburg, *Ann.*, **203**, 241 (1880).
70. C. Pape, *Ber.*, **14**, 1874 (1881).
71. A. Polis, *Ber.*, **19**, 1012 (1886).
72. —, *Ber.*, **19**, 1024 (1886).
73. L. Gatterman and E. Ellery, *Ber.*, **32**, 1114 (1899).
74. W. Dilthey, and F. Eduardoff, *Ber.*, **37**, 1139 (1904).
75. —, *Ber.*, **38**, 4132 (1905).
76. A. Ladenburg, *Ber.*, **40**, 2274 (1907).
77. —, *Ber.*, **41**, 966 (1908).
78. W. Melzer, *Ber.*, **41**, 3390 (1908).
79. G. Martin, *J. Chem. Soc.*, **105**, 2836 (1914).
80. W. Schlenk, J. Renning and G. Racky, *Ber.*, **44**, 1178 (1911).
81. G. Martin, *Ber.*, **45**, 403 (1912).
82. W. Schlenk, *Ann.*, **394**, 221 (1912).
83. H. Jörg and J. Stetter, *J. prakt. Chem.* **117**, 305 (1927).
84. H. W. Post, "The Chemistry of Aliphatic Orthoesters," Reinhold Publishing Corp., New York, 1943.
85. C. A. Kraus and W. K. Nelson, *J. Am. Chem. Soc.*, **56**, 195 (1934).
86. F. Taurke, *Ber.*, **38**, 1661 (1905).
87. C. Friedel and J. Crafts, *Ann. chim. phys.*, (*4*), **19**, 337 (1870).
88. W. C. Schumb and C. M. Saffer, Jr., *J. Am. Chem. Soc.*, **61**, 363 (1939).
89. R. Schwarz and W. Sexauer, *Ber.*, **59B**, 333 (1926).
90. A. Bygden, *Ber.*, **45**, 707 (1912).
91. W. C. Schumb and C. M. Saffer, Jr., *J. Am. Chem. Soc.*, **63**, 93 (1941).
92. E. G. Rochow and W. F. Gilliam, J. Am. Chem. Soc., **63**, 798 (1941).
93. W. C. Schumb, J. Ackerman and C. M. Saffer, Jr., *ibid.*, **60**, 2486 (1938).

94. A. Tschitschibabin and S. Jelgasin, *Ber.*, **47**, 48 (1914).
95. W. F. Gilliam, H. A. Liebhafsky and A. F. Winslow, *J. Am. Chem. Soc.*, **63**, 801 (1941).
96. J. F. Hyde and R. C. DeLong, *ibid.*, **63**, 1194 (1941).
97. G. Martin, *Ber.*, **46**, 2442 (1913).
98. A. Stock and C. Somieski, *Ber.*, **52B**, 695 (1919).
99. General Electric Co., U. S. Patent 2258218 (1941).
100. —,   "   2258219 (1941).
101. —,   "   2258220 (1941).
102. —,   "   2258221 (1941).
103. —,   "   2258222 (1941).
104. —,   "   2286763 (1941).
105. British Thomson-Houston Co., Ltd., British Patent 548911 (1942).
106. —,   "   548912 (1942).
107. —,   "   549081 (1942).
108. General Electric Co., U. S. Patent 2306222 (1942).
109. British Thomson-Houston Co., Ltd., British Patent 551649 (1943).
110. —,   "   552640 (1943).
111. General Electric Co., U. S. Patent 2352974 (1944).
112. W. R. Collings, *Chem. Eng. News*, **23**, 1616 (1945).
113. Corning Glass Works, U. S. Patent 2371050 (1945).
114. General Electric Co., U. S. Patent 2371068 (1945).
115. Dow Corning Co., Private Communication (1945).
116. General Electric Co., U. S. Patent 2381137 (1945).
117. A. Stock and C. Somieski, *Ber.*, **51**, 989 (1918).
118. C. Friedel and J. Crafts, *Ann. chim. phys.* (*4*), **9**, 5 (1866).
119. General Electric Co., U. S. Patent 2381138 (1945).
120. —,   "   2381139 (1945).
121. —,   "   2381366 (1945).
122. Corning Glass Works, U. S. Patent 2384384 (1945).
123. —,   "   2386467 (1945).
124. —,   "   2386488 (1945).
125. American Cyanamid Co., U. S. Patent 2388161 (1945).
126. Corning Glass Works, U. S. Patent 2386452 (1945).
127. E. I. du Pont de Nemours and Co., U. S. Patent 2386793 (1945).
128. D. Peppard, W. Brown and W. Johnson, *J. Am. Chem. Soc.*, **68**, 70 (1946).
129. —, —, —, *ibid.*, **68**, 73 (1946).
130. —, —, —, *ibid.*, **68**, 76 (1946).
131. —, —, —, *ibid.*, **68**, 77 (1946).
132. R. Sauer, *J. Am. Chem. Soc.*, **68**, 138 (1946).
133. M. Hunter, J. F. Hyde, E. Warrick and H. Fletcher, *J. Am. Chem. Soc.*, **68**, 667 (1946).
134. Pittsburgh Plate Glass Co., U. S. Patent 2394642 (1946).
135. L. Troost and P. Hautefeuille, *Bull. soc. chim.* (*2*) **13**, 213 (1870).
136. —, —, *ibid.*, **16**, 240 (1871).
137. —, —, *ibid.*, **19**, 225 (1873).
138. —, —, *ibid.*, **35**, 360 (1881).
139. H. Reinboldt and W. Wisfeld, *J. prakt. Chem.*, **142**, 23 (1935).
140. L. Troost and P. Hautefeuille, *Ann. chim. phys.* (*5*), **7**, 452 (1876).
141. H. Reinboldt and W. Wisfeld, *Ann.*, **517**, 197 (1935).
142. W. Schumb and C. Klein, *J. Am. Chem. Soc.*, **59**, 261 (1937).

143. W. Schumb and D. Holloway, *ibid.*, **63**, 2753 (1941).
144. A. Stock and C. Somieski, *Ber.*, **50**, 1379 (1917).
145. —, C. Somieski and R. Wintgen, *Ber.*, **50**, 1754 (1917).
146. —, *Ber.*, **50**, 1769 (1917).
147. —, C. Somieski and R. Wintgen, *Ber.*, **50**, 1764 (1917).
148. —, *Ber.*, **50**, 169 (1917).
149. —, *Ber.*, **50**, 171 (1917).
150. —, *Ber.*, **50**, 108 (1917).
151. —, and C. Somieski, *Ber.*, **49**, 111 (1916).
152. E. G. Rochow, *J. Am. Chem. Soc.*, **67**, 963 (1945).
153. General Electric Co., U. S. Patent 2380995 (1945).
154. —,   "   2380996 (1945).
155. —,   "   2380997 (1945).
156. —,   "   2380998 (1945).
157. —,   "   2380999 (1945).
158. —,   "   2381000 (1945).
159. —,   "   2381001 (1945).
160. —,   "   2381002 (1945).
161. E. I. du Pont de Nemours and Co., U. S. Patent 2379821 (1945).
162. General Electric Co., U. S. Patent 2383818 (1945).
163. J. E. Reynolds, *Chem. News*, **100**, 245 (1909); *C. A.*, **4**, 426 (1910).
164. L. Troost and P. Hautefeuille, *Ann. chim. phys.* (5), **7**, 459 (1876).
165. L. Gatterman, *Ber.*, **22**, 186 (1889).
166. —, and K. Weinlig, *Ber.*, **27**, 1943 (1894).
167. A. Besson and L. Fournier, *Compt. rend.*, **148**, 555 (1909).
168. —, —, *ibid.*, **148**, 839 (1909).
169. —, —, *ibid.*, **149**, 34 (1909).
170. W. Schumb and E. Gamble, "Inorganic Syntheses," Vol. 1, p. 42.   McGraw Hill Book Co., New York, 1939.
171. J. Gierut, F. Sowa and J. Nieuwland, *J. Am. Chem. Soc.*, **58**, 897 (1936).
172. —, —, —, *ibid.*, **58**, 786 (1936).
173. W. Schumb and H. Anderson, *ibid.*, **58**, 994 (1936).
174. H. Booth and C. Swinehart, *ibid.*, **54**, 4750 (1932).
175. —, —, *ibid.*, **57**, 1333 (1935).
176. E. Flood and L. Horowitz, *ibid.*, **55**, 2534 (1933).
177. B. Dolgov and Y. Vol'nov, *Zuhr. Obshchei Khim.*, Ser., **1**, 91 (1931); *C.A.*, **25**, 4535 (1931).
178. J. Quig, *Iowa State College J. Sci.*, **6**, 467 (1932).
179. W. Schumb and R. C. Young, *J. Am. Chem. Soc.*, **52**, 1464 (1930).
180. Deutsche Gold- und Silber-Scheideanstalt vorm. Roessen, German Patent 467637; *C.A.*, **23**, 939 (1929).
181. V. Ipatieff and B. Dolgov, *Ber.*, **62**, 1220 (1929).
182. A. Besson and L. Fournier, *Compt. rend.*, **152**, 603 (1911).
183. —, —, *ibid.*, **151**, 1055 (1910).
184. K. Adwentowski and E. Drozdowski, *Bull. intern. acad. sci.*, *Cracowie* (A), 330 (1911); *C.A.*, **6**, 1722 (1912).
185. A. Besson, *Compt. rend.*, **151**, 1603 (1912).
186. J. Zanetti, *J. Am. Chem. Soc.*, **34**, 1598 (1912).
187. C. Sanger and E. R. Riegel, *Proc. Am. Acad. Sci.*, **48**, 573 (1913).
188. G. Grüttner and E. Krause, *Ber.*, **50**, 1559 (1917).
189. A. Landenburg, *Ber.*, **7**, 387 (1874).

190. O. Hutchins, Canadian Patent 184354 (1918).
191. —, U. S. Patent 1271713 (1918).
192. G. Grüttner and M. Cauer, *Ber.*, **51**, 1283 (1918).
193. R. Wintgen, *Ber.*, **52**, 724 (1919).
194. A. Stock and K. Somieski, *Ber.*, **52**, 1851 (1919).
195. A. Bygden, Inaugural Diss., Uppsala, Sweden (1916); *C.A.*, **14**, 1974 (1920).
196. R. Moore, U. S. Patent 1350932 (1919).
197. A. Stock, *Chem. Zeitung*, **43**, 594 (1919).
198. R. Schwartz and O. Liede, *Ber.*, **53**, 1860 (1920).
199. A. Stock and K. Somieski, *Ber.*, **53**, 759 (1920).
200. —, —, *Ber.*, **54**, 740 (1921).
201. Consortium für Elektrochemische Industrie-Ges., British Patent 175811 (1922).
202. E. Krause and G. Renwanz, *Ber.*, **62**, 1710 (1929).
203. H. H. Reynolds, L. A. Bigelow and C. A. Kraus, *J. Am. Chem. Soc.*, **51**, 3067 (1929).
204. Chao-Lun Tseng and Tsung-Yi Chao, *Sci. Reports Natl. U. Pieping*, **1** (No. 4) 21 (1936); *C.A.*, **31**, 655 (1937).
205. P. Budnikov and E. Shilov, *C.A.*, **20**, 1550 (1926).
206. D. F. Helm and E. Mack, Jr., *J. Am. Chem. Soc.*, **59**, 60 (1937).
207. W. C. Schumb and H. H. Anderson, *ibid.*, **59**, 651 (1937).
208. R. Schwarz and H. Meckbach, *Z. anorg. allgem. Chem.*, **232**, 241 (1937); *C.A.*, **31**, 5704 (1937).
209. —, and G. Pietsch, *ibid.*, **232**, 249 (1937); *C.A.*, **31**, 5705 (1937).
210. R. L. Livingston and L. O. Brockway, *J. Am. Chem. Soc.*, **66**, 94 (1944).
211. H. V. Medoks and N. Z. Kotelkov, *ibid.*, **7**, 2007 (1937); *C.A.*, **32**, 531 (1938).
212. S. N. Ushakov and A. M. Itenberg, *J. Gen. Chem.*, *U.S.S.R.*, **7**, 2495 (1937); *C.A.*, **32**, 2083 (1938).
213. I. G. Farbenindustrie, French Patent 822350 (1937).
214. H. V. Medoks, *J. Gen. Chem.*, *U.S.S.R.*, **8**, 291 (1938); *C.A.*, **32**, 5392 (1938).
215. E. M. Soshestvenskaya, *ibid.*, **8**, 294 (1938); *C.A.*, **32**, 5392 (1938).
216. R. Schwarz, *Angew. Chem.*, **51**, 238 (1938).
217. A. G. Maddock, C. Reid and H. J. Emeleus, *Nature*, **144**, 328 (1939).
218. R. Schwarz and U. Gregor, *Z. anorg. allgem. Chem.*, **241**, 395 (1939); *C.A.*, **34**, 1267 (1940).
219. G. Calingaert, H. Soroos and V. Hnizda, *J. Am. Chem. Soc.*, **62**, 1107 (1940).
220. M. M. Koton, *J. App. Chem.*, *U.S.S.R.*, **12**, 1435 (1939); *C.A.*, **34**, 6262 (1940).
221. E. L. Niedzielski, *J. Am. Chem. Soc.*, **62**, 3519 (1940).
222. K. A. Andrianov, *Compt. rend. acad. sci. U.R.S.S.*, **28**, 66 (1940); *C.A.*, **35**, 2431 (1941).
223. E. I. du Pont de Nemours and Co., U. S. Patent 2238669 (1941).
224. Y. Vol'nov and A. Reutt, *J. Gen. Chem.*, *U.S.S.R.*, **10**, 1600 (1940); *C.A.*, **35**, 2853 (1941).
225. E. M. Soshestvenskaya, *ibid.*, **10**, 1689 (1940); *C.A.*, **35**, 3240 (1941).
226. Z. M. Manulkin and F. Yakubova, *ibid.*, **10**, 1300 (1940); *C.A.*, **35**, 3240 (1941).
227. H. J. Emeleus, A. G. Maddock and C. Reid, *J. Chem. Soc.*, 353 (1941).
228. W. C. Schumb, "Inorganic Syntheses," Vol. 1, p. 38. McGraw Hill Book Co., New York, 1939.
229. R. Schwarz and A. Pflugmacher, *Ber.*, **75B**, 1062 (1942).
230. A. C. Taylor and B. V. de G. Walden, *J. Am. Chem. Soc.*, **66**, 842 (1944).
231. K. Kitaoka, Japanese Patent 101515; *C.A.*, **28**, 5186 (1934).
232. H. S. Booth and W. D. Stilwell, *J. Am. Chem. Soc.*, **56**, 1529 (1934).

233. H. S. Booth and W. D. Stilwell, *ibid.*, **56**, 1531 (1934).
234. H. Buff and F. Wöhler, *Ann.*, **104**, 94 (1857).
235. F. Wöhler and H. Buff, *Ann.*, **103**, 218 (1857).
236. A. Bygden, *Ber.*, **44**, 2642 (1911).
237. G. Martin, *Ber.*, **45**, 2097 (1912).
238. C. Combes, *Compt. rend.*, **122**, 531 (1896).
239. —, *Bull. soc. chim.* (*3*), **7**, 242 (1892).
240. O. Ruff and C. Albert, *Ber.*, **38**, 53 (1905).
241. —, —, *Ber.*, **38**, 2222 (1905).
242. O. Hutchins, *Trans. Am. Electrochemical Soc.*, **35** (preprint).
243. G. Richter, *ibid.*,   **35** ("   ).
244. A. Stock and F. Zeidler, *Ber.*, **56**, 986 (1923).
245. —, and C. Somieski, *Ber.*, **56**, 250 (1923).
246. E. G. Rochow and F. Norton, *Colloid Chem.*, **6**, 1093 (1946); *C.A.*, **40**, 2435 (1946).
247. General Electric Co., U. S. Patent 2390378 (1945).
248. —,   "   2389477 (1945).
249. Corning Glass Works, U. S. Patent 2389802 (1945).
250. —,   "   2389804 (1945).
251. —,   "   2389805 (1945).
252. —,   "   2389806 (1945).
253. —,   "   2389807 (1945).
254. —,   "   2389803 (1945).
255. —,   "   2380057 (1945).
256. H. N. Warren, *Chem. News*, **60**, 158 (1889).
257. General Electric Co., U. S. Patent 2389931 (1945).
258. F. C. Whitmore, L. H. Sommer, P. D. DiGiorgio, W. A. Strong, R. E. Van Strien, D. L. Bailey, H. K. Hall, E. W. Pietrusza and G. T. Kerr, *J. Am. Chem. Soc.*, **68**, 475 (1946).
259. F. C. Whitmore and L. H. Sommer, *ibid.*, **68**, 481 (1946).
260. L. H. Sommer and F. C. Whitmore, *ibid.*, **68**, 485 (1946).
261. —, E. Dorfman, G. M. Goldberg and F. C. Whitmore, *ibid.*, **68**, 488 (1946).
262. W. I. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).
263. D. W. Scott, *ibid.*, **68**, 356 (1946).
264. E. I. du Pont de Nemours and Co., U. S. Patent 2395880 (1946).
265. Corning Glass Works, British Patent 563995 (1944).
266. R. O. Sauer, W. J. Scheiber and S. D. Bremer, *J. Am. Chem. Soc.*, **68**, 962 (1946).
267. T. Alfrey, F. J. Honn and H. Mark, *J. Polymer Sci.*, **1**, 102 (1946).
268. Imperial Chemical Industries, U. S. Patent 2396692 (1946).
269. Corning Glass Works, U. S. Patent 2397895 (1946).
270. General Electric Co., U. S. Patent 2398672 (1946).
271. L. H. Sommer, G. M. Goldberg, E. Dorfman and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 1083 (1946).
272. H. R. Simonds, M. H. Bigelow and J. V. Sherman, "The New Plastics," D. Van Nostrand Co., New York, 1945.
273. F. J. Norton, *General Electric Review*, August 2, 1944.
274. S. L. Bass, J. F. Hyde, E. C. Britton and R. R. McGregor, *The Laboratory*, **15**, (No. 2) 42 (1944).
275. Dow Corning Co., "Dow Corning Resins 993 and 2052".
276. —, "Dow Corning Fluids".
277. —, *Plastics*, **2**, 40 (1945).
278. —, "Dow Corning Ignition and Sealing Compounds".

279. E. G. Rochow, *Chem. Eng. News*, **23**, 612 (1945).
280. General Electric Co., "Silicone Rubber".
281. H. A. Gardner and M. W. Westgate, *Chem. Eng. News*, **23**, 1082 (1945).
282. Dow Corning Co., "Dow Corning Silicones" (1945).
283. Carbide and Carbon Chemicals Corp., Private Communication (1946).
284. H. W. Post and C. H. Hofrichter, Jr., *J. Org. Chem.*, **5**, 572 (1940).
285. Houde Engineering Div., Houdaille-Hershey Corp., Private Communication (1946).
286. R. F. Horrell, *Plastics*, **4**, 50 (1946).
287. H. E. Fritz, *Chem. Eng. News*, **24**, 1570 (1946).
288. R. O. Sauer, *J. Chem. Ed.*, **21**, 303 (1944).
289. Nomenclature, Spelling and Pronunciation Committee, A.C.S., *Chem. Eng. News*, **24**, 1233 (1946).
290. H. Hausmann, *J. Chem. Ed.*, **23**, 16 (1946).
291. H. J. Emeleus and C. J. Wilkins, *J. Chem. Soc.*, **454**)1944).
292. C. Friedel and A. Ladenburg, *Ann.*, **159**, 262 (1871).
293. W. Knop, *J. prakt. Chem.* **74**, 41 (1858).
294. W. Dilthey, *Ber.*, **36**, 923 (1903).
295. —, *Ber.*, **36**, 1595 (1903).
296. —, *Ber.*, **36**, 3207 (1903).
297. —, *Ann.*, **344**, 305 (1905).
298. A. von Baeyer and V. Williger, *Ber.*, **35**, 3013 (1902).
299. S. Uchida and T. Kondo, *J. Soc. Chem. Ind. Japan*, **36** (Suppl. binding) 190 (1933); *C.A.*, **27**, 3464 (1933).
300. E. I. du Pont de Nemours and Co., U. S. Patent 2048799 (1936).
301. G. Klein and H. Nienburg, *Ber.*, **69**, 2066 (1936).
302. I. G. Farbenindustrie, German Patent 637532 (1936).
303. Byk-Guldenwerke Chem. Fabrik, German Patent 662732 (1938).
304. Y. N. Vol'nov, *J. Gen. Chem.*, *U.S.S.R.*, **10**, 1717 (1940); *C.A.*, **35**, 3963 (1941).
305. M. N. Kalinin, *Compt. rend. acad. sci. U.R.S.S.*, **28**, 365 (1940); *C.A.*, **35**, 2470 (1941).
306. H. J. Backer and H. A. Klasens, *Rec.`trav. chim.*, **61**, 500 (1942).
307. H. A. Klasens and H. J. Backer, *ibid.*, **61**, 513 (1942).
308. H. J. Backer and H. A. Klasens, *ibid.*, **61**, 802 (1942).
309. R. O. Sauer, *J. Am. Chem. Soc.*, **66**, 1707 (1944).
310. Y. N. Vol'nov and A. Mishelevich, *J. Gen. Chem.*, *U.S.S.R.*, **13**, 213 (1943); *C.A.*, **38**, 1484 (1944).
311. R. O. Sauer and R. N. Hasek, *J. Am. Chem. Soc.*, **68**, 241 (1946).
312. H. J. Emeleus and N. Miller, *J. Chem. Soc.*, 819 (1939).
313. —, —, *Nature*, **142**, 996 (1938).
314. P. A. DiGiorgio, L. H. Sommer and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 344 (1946).
315. W. F. Gilliam and R. O. Sauer, *ibid.*, **66**, 1793 (1944).
316. R. I. Shtetter, Russian Patent 44934; *C.A.*, **32**, 2958 (1938).
317. J. E. Reynolds, *J. Chem. Soc.*, **55**, 474 (1889).
318. A. Bygden, *Ber.*, **48**, 1236 (1915).
319. W. B. Hart, *Jahresberichte*, 1943 (1889).
320. J. E. Reynolds, *J. Chem. Soc.*, **53**, 853 (1888).
321. C. A. Kraus and R. Rosen, *J. Am. Chem. Soc.*, **47**, 2739 (1925).
322. A. Harden, *J. Chem. Soc.*, **51**, 40 (1887).

323. J. E. Reynolds, *J. Chem. Soc.*, **51**, 203 (1887).
324. C. A. Kraus and H. Eatough, *J. Am. Chem. Soc.*, **55**, 5008 (1933).
325. G. Constabaris, *Chem. Eng. News*, **24**, 2268 (1946).
326. Minnesota Mining and Manufacturing Co., Private Communication.
327. Chemische Fabrik von Heyden, German Patent 743222 (1943).
328. L. Holzapfel, J. Kerner and H. Neuhaus, *Glastech. Ber.*, **21**, 13 (1943); *C.A.*, **39**, 2051 (1945).
329. C. A. Burkhard, *J. Am. Chem. Soc.*, **67**, 2173 (1945).
330. —, B. F. Decker and H. Harker, *J. Am. Chem. Soc.*, **67**, 2174 (1945).
331. L. K. Frevel and M. J. Hunter, *ibid.*, **67**, 2275 (1945).
332. L. Holzapfel and I. Kerner-Esser, *Naturwiss.*, **31**, 386 (1943); *C.A.*, **38**, 2376 (1944).
333. —, *Kolloid Z.*, **100**, 380 (1942); *C.A.*, **38**, 4251 (1944).
334. —, *Naturwiss.*, **30**, 185 (1942); *C.A.*, **36**, 5237 (1942).
335. —, *Z. Elek.*, **47**, 327 (1941); *C.A.*, **35**, 5377 (1941).
336. J. E. Brophy, R. O. Millitz and W. A. Zisman, *Trans. Am. Soc. Mech. Eng.*, **68**, 355 (1946).
337. V. G. Fitzsimmons, D. L. Pickett, and R. O. Millitz, *ibid.*, **68**, 361 (1946).
338. H. Gilman and S. P. Massie, Jr., *J. Am. Chem. Soc.*, **68**, 1128 (1946).
339. H. N. Warren, *Chem. News*, **66**, 113 (1892).
340. H. D. Cogan and C. A. Setterstrom, *Chem. Eng. News*, **24**, 2499 (1946).
341. General Electric Co., *Chem. Eng. News*, **24**, 2532 (1946).
342. L. Troost and P. Hautefeuille, *Bull. soc. chim.* (*2*), **19**, 249 (1873).
343. Corning Glass Works, U. S. Patent 2377689 (1945).
344. Synthetic Plastics Co., U. S. Patent 1178731 (1916).
345. Westinghouse Electric and Mfg. Co., U. S. Patent 2377600 (1945).
346. D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 691 (1946).
347. C. Pape, *Ann.*, **222**, 355 (1884).
348. F. Wöhler, *Ann.*, **127**, 257 (1863).
349. E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, New York, 1946.
350. G. Martin, *Ber.*, **46**, 3289 (1913).
351. D. T. Hurd and E. G. Rochow, *J. Am. Chem. Soc.*, **67**, 1057 (1945).
352. C. E. Waring, *Trans. Faraday Soc.*, **36**, 1142 (1940).
353. General Electric Co., *Chem. Eng. News*, **24**, 2831 (1946).
354. D. T. Hurd, *J. Am. Chem. Soc.*, **67**, 1545 (1945).
355. R. O. Sauer and W. I. Patnode, *ibid.*, **67**, 1548 (1945).
356. E. G. Rochow and W. F. Gilliam, *ibid.*, **67**, 1772 (1945).
357. D. T. Hurd, *ibid.*, **67**, 1813 (1945).
358. E. I. du Pont de Nemours and Co., U. S. Patent 2395550 (1946).
359. L. Troost and P. Hautefeuille, *Bull. soc. chim.* (*2*), **19**, 255 (1873).
360. Byk-Guldenwerke Chem. Fabrik, German Patent 625077 (1938).
361. P. A. DiGiorgio, W. A. Strong, L. H. Simmons and F. C. Whitmore, *J. Am. Chem. Soc.*, **68**, 1380 (1946).
362. R. N. Meals, *ibid.*, **68**, 1880 (1946).
363. L. H. Simmons, D. L. Bailey, W. A. Strong and F. C. Whitmore, *ibid.*, **68**, 1881 (1946).
364. E. I. du Pont de Nemours and Co., British Patent 542166 (1941).
365. General Electric Co., *Chem. Eng. News*, **24**, 3086 (1946).
366. British Thomson-Houston Co., Ltd., British Patent 544143 (1942).
367. F. S. Kipping, *Proc. Chem. Soc.*, **20**, 15 (1904).
368. —, and L. L. Lloyd, *Proc. Chem. Soc.*, **15**, 174 (1899).

369. Corning Glass Works, U. S. Patent 2375998 (1945).
370. —,   " 2382082 (1945).
371. —,   " 2386441 (1945).
372. —,   " 2386466 (1945).
373. —,   " 2390518 (1945).
374. —,   " 2397727 (1946).
375. —,   " 2398187 (1946).
376. F. J. Stark, G. H. Slack, R. M. Ruthledge and H. A. Hirst, U. S. Patent 2399697 (1946).
377. R. R. McGregor, *J. Franklin Inst.*, **242** (No. 2) 93 (1946).
378. General Electric Co., U. S. Patent 2383827 (1945).
379. —,   " 2386259 (1945).
380. —,   " 2388299 (1945).
381. —,   " 2388575 (1945).
382. —,   " 2392713 (1945).
383. —,   " 2394040 (1946).
384. Corning Glass Works, U. S. Patent 2410346 (1946).
385. General Electric Co., U. S. Patent 2405041 (1946).
386. —,   " 2406605 (1946).
387. —,   " 2406621 (1946).
388. —,   " 2408822 (1946).
389. L. O. Brockway and F. T. Wall, *J. Am. Chem. Soc.*, **56,** 2373 (1934).
390. —, and H. O. Jenkins, *ibid.*, **58,** 2036 (1936).
391. —, and N. R. Davidson, *ibid.*, **63,** 3287 (1941).
392. R. L. Livingston and L. O. Brockway, *J. Am. Chem. Soc.*, **68,** 719 (1946).
393. R. W. Kolderman, *Can. Chem. Proc. Ind.*, **29,** 147 (1945).
394. F. S. Kipping, *Proc. Roy. Soc.*, **A159,** 139 (1937).
395. H. S. Booth and P. H. Carwell, *J. Am. Chem. Soc.*, **68,** 2650 (1946).
396. —, and H. S. Halbedel, *ibid.*, **68,** 2652 (1946).
397. —, and W. F. Martin, *ibid.*, **68,** 2655 (1946).
398. —, and J. F. Suttle, *ibid.*, **68,** 2658 (1946).
399. —, and D. R. Spessard, *ibid.*, **68,** 2660 (1946).
400. —, and A. A. Schwartz, *ibid.*, **68,** 2662 (1946).
401. H. Gilman, R. N. Clark, R. E. Wiley and H. Diehl, *ibid.*, **68,** 2728 (1946).
402. Dow Corning Corp., *Chem. Eng. News,* **22,** 1134 (1944).
403. —, *Chem. Met. Eng.*, **51,** 138 (1944).
404. F. M. Jaeger and D. W. Dijkstra, *Verslag Akad. Wetenschappen (Amsterdam)*, **33,** 333 (1924); *C.A.*, **18,** 3533 (1924).
405. —, —, *ibid.*, **27,** 393 (1924); *C.A.*, **19,** 209 (1925).
406. —, —, *Z. anorg. allgem. Chem.*, **143,** 233 (1925); *C.A.*, **19,** 2448 (1925).
407. G. Grüttner and M. Wiernik, *Ber.*, **45,** 1474 (1912).
408. A. Ladenburg, *Ber.*, **6,** 379 (1873).
409. S. Sugden and H. Wilkins, *J. Chem. Soc.*, 126 (1931).
410. E. A. Flood, *J. Am. Chem. Soc.*, **55,** 1735 (1933).
411. E. Khotinsky, *Ber.*, **41,** 3088 (1909).
412. —, and B. Seregenkoff, *Ber.*, **41,** 2946 (1908).
413. C. Friedel and A. Ladenburg, *Compt. rend.*, **68,** 920 (1869).
414. J. B. Dumas, *Compt. rend.*, **10,** 149 (1840).
415. B. Dolgov and J. Wolnov, *J. Russ. Phys. Chem. Soc.*, **63,** 91 (1931).
416. R. R. Widdowson, *J. Chem. Soc.*, 958 (1926).

417. E. Krause and A. von Grosse, "Die Chemie der Metall-organischen Verbindungen," Edwards Bros., Ann Arbor, Mich., 1943.
418. V. Ipatieff and B. Dolgov, *J. Russ. Phys. Chem. Soc.*, **63**, 5 (1931).
419. A. Bygden, *Z. phys. Chem.*, **90**, 246 (1915).
420. Dow Corning Co., Bulletin 1-A "Silastic" (1946).
421. C. A. Burkhard, *J. Am. Chem. Soc.*, **68**, 2103 (1946).
422. M. Manulkin, *J. Gen. Chem.*, *U.S.S.R.*, **16**, 235 (1936); *C.A.*, **41**, 80 (1947).
423. I. G. Farbenindustrie, German Patent 697420 (1940).
424. L. Knorr and H. Wieland, German Patent 285285 (1915).
425. I. G. Farbenindustrie, German Patent 598667 (1930).
426. I. G. Farbenindustrie, German Patent 660075 (1938).
427. M. J. Hunter, E. L. Warrick, J. F. Hyde and C. C. Currie, *J. Am. Chem. Soc.*, **68**, 2284 (1946).
428. S. L. Bass, J. F. Hyde and R. R. McGregor, *J. Am. Ceramic Soc.*, **29**, 66 (1946).
429. —, M. J. Hunter and T. A. Kauppi, *Trans. Electroch. Soc.*, **90**, 255 (1946).
430. T. A. Kauppi and G. L. Moses, *Trans. Am. Inst. Elec. Eng.*, **64**, 1 (1945).
431. S. L. Bass and T. A. Kauppi, *Proc. I.R.E.*, **33**, 441 (1945).
432. A. E. Newkirk, *J. Am. Chem. Soc.*, **68**, 2736 (1946).
433. C. B. Hurd, *ibid.*, **68**, 364 (1946).
434. R. O. Sauer, ibid., **68**, 954 (1946).
435. W. F. Gilliam, R. N. Meals and R. O. Sauer, *ibid.*, **68**, 1161 (1946).
436. R. O. Sauer and D. J. Mead, *ibid.*, **68**, 1794 (1946).
437. D. W. Scott, *ibid.*, **68**, 1877 (1946).
438. L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.*, **68**, 2282 (1946).
439. E. L. Warrick, *ibid.*, **68**, 2455 (1946).
440. British Thomson-Houston Co., Ltd., British Patent 542655 (1942).
441. Corning Glass Works, British Patent 561136 (1944).
442. —, U. S. Patent 2390370 (1945).
443. A. Abati, *Z. phys. Chem.*, **25**, 353 (1898).
444. J. von Ebelman, *Ann.*, **57**, 331 (1846).
445. Carbide and Carbon Chemicals Corp., *Chem. Eng. News*, **25**, 636 (1947).
446. R. N. Lewis, *J. Am. Chem. Soc.*, **69**, 717 (1947).
447. L. B. Falkenburg, H. M. Teeter and J. C. Craven, *J. Am. Chem. Soc.*, **69**, 486 (1947).
448. J. F. Hyde, L. K. Frevel, H. S. Nutting, P. S. Petrie and M. A. Purcell, *J. Am. Chem. Soc.*, **69**, 488 (1947).
449. H. Gilman and R. N. Clark, *ibid.*, **68**, 1675 (1946).
450. W. H. Pearlson, T. J. Brice and J. H. Simons, *ibid.*, **67**, 1769 (1945).
451. R. H. Krieble and J. R. Elliott, *ibid.*, **67**, 1810 (1945).
452. W. I. Patnode and F. C. Schmidt, *ibid.*, **67**, 2272 (1945).
453. L. H. Sommer, E. W. Pietrusza, G. T. Kerr and F. C. Whitmore, *ibid.*, **68**, 156 (1946).
454. B. Smith, *Svensk Kem. Tids.*, **58** 150 (1946); *C.A.*, **40**, 6319 (1946).
455. E. W. Balis and H. A. Liebhasky, *Ind. Eng. Chem.*, **38**, 583 (1946).
456. Polaroid Corp., U. S. Patent 2397287 (1946).
457. C. A. Scarlott, *Westinghouse Eng.*, **5**, 130 (1945).
458. Plax Corp., U. S. Patent 2405019 (1946).
459. Shell Development Co., U. S. Patent 2406671 (1946).
460. General Electric Co., U. S. Patent 2403370 (1946).
461. S. R. Robinson, *Sci. J. Roy. Coll. Sci.*, **15**, 24 (1945).
462. J. Marsden. *Rubber Age* (*N. Y.*), **59**, 691 (1946).

463. F. J. Sowa, U. S. Patent 2407037 (1946).
464. W. S. Penn, *Paint Manuf.*, **15**, 364 (1945).
465. A. P. Kreshkov, and G. S. Petrov, *Khim. Prom.*, **10** (No. 8) (1944); *C. A.*, **40**, 1689 (1946).
466. T. A. Kauppi and W. W. Pedersen, *S.A.E. Journal*, **54** 120T (1946).
467. R. F. Field, *J. Applied Physics*, **17** 318 (1946).
468. W. R. Collings, *Trans. Am. Inst. Chem. Eng.*, **42**, 455 (1946).
469. D. L. Loughborough and E. G. Haas, *J. Aeronaut. Sci.*, **13** (No. 3) 126 (1946).
470. J. F. Macphearson, *A.S.T.M. Bull.*, No. 140, 63 (1946).
471. T. A. Kauppi, *Inst. Spokesman*, **10** (No. 13) 1 (1946).
472. F. Mohler, *Iron Steel Engr.*, **23** (No. 7) 59 (1946).
473. M. de Buccar, *Inds. Plastiques*, **2**, 8 (1946).
474. —, *ibid.*, **2**, 49 (1946).
475. J. R. Patterson, Official Dig. Fed. Paint and Varnish Produc. Clubs, (No. 258) 281 (1946).
476. H. G. Emblem, *Paint Manuf.*, **16**, 291 (1946).
477. S. B. Morris, *J. Am. Waterworks Assoc.*, **38**, 993 (1946).
478. H. A. Knight, *Materials and Methods*, **22**, 1069 (1945).
479. E. E. Marbaker, *J. Am. Ceramic Soc.*, **28**, 329 (1945).
480. Monsanto Chemical Co., U. S. Patent 2389491 (1945).
481. A. Koff and M. Frederick, *Ind. Eng. Chem., Anal. Ed.*, **17**, 745 (1945).
482. T. A. Kauppi, G. Grant, G. L. Moses and R. F. Horell, *Westinghouse Engineer*, **5**, 135 (1945).
483. R. F. Horell, *Paper Trade J.*, **121**, (No. 22) 18 (1945).
484. Chicago Paint and Varnish Club, *Am. Paint J.*, **30** (No. 6A), 7 (1945).
485. P. O. Powers, *Nat. Paint Bull.*, **9** (No. 10) 5 (1945).
486. T. A. Kauppi and W. W. Pedersen, *Nat. Pet. News*, **37**, 944 (1945).
487. C. A. Scarlott, *Plastics and Resins*, (No. 2), **7** (1946).
488. Cities Service Oil Co., U. S. Patent 2398662 (1946).
489. W. S. Penn, *Plastics (London)*, **9**, 273 (1945).
490. G. P. Brown, *Rev. Sci. Instruments*, **16**, 316 (1945).
491. K. A. Andrianov, *Khim. Prom.*, (No. 2) 1 (1945): *C.A.*, **40**, 2352 (1946).
492. P. C. Servais, *Rubber Age (N. Y.)*, **58**, 579 (1946).
493. W. S. Penn, *India Rubber J.*, **109**, 625 (1945).
494. Shell Development Co., U. S. Patent 2375007 (1945).
495. L. V. Larsen, J. J. Whelton and J. J. Pyle, *Modern Plastics*, **23**, (No. 6), 160 (1946).
496. H. H. Anderson, *J. Am. Chem. Soc.*, **67**, 2176 (1945).
497. G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **67**, 1911 (1945).
498. F. J. Sowa, U. S. Patent 2383521 (1945).
499. General Electric Co., U. S. Patent 2383817 (1945).
500. E. Davis, *Pacific Plastics*, **3** (No. 6), 28 (1945).
501. E. Davis, *Pacific Plastics*, **3** (No. 7) 40 (1945).
502. A. Black, *Mech. Eng.*, **67**, 190 (1945).
503. E. R. Weidlein, *Chem. Eng. News*, **23**, 520 (1945).
504. H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, **69**, 967 (1947).
505. L. H. Sommer, G. M. Goldberg, J. Gold and F. C. Whitmore, *J. Am. Chem. Soc.*, **69**, 980 (1947).
506. L. J. Tyler, L. H. Sommer and F. C. Whitmore, *ibid.*, **69**, 981 (1947).
507. Corning Glass Works, British Patent 571725 (1945).
508. —, " 574653 (1946).
509. —, " 579408 (1946).

510. G. S. Forbes and H. H. Anderson, *J. Am. Chem. Soc.*, **66**, 1703 (1944).
511. —, —, *ibid.*, **62**, 761 (1940).
512. H. H. Anderson, *ibid.*, **66**, 934 (1944).
513. P. Miquel, *Ann. chim. phys.* (*5*), **11**, 343 (1877).
514. J. E. Reynolds, *J. Chem. Soc.*, **89**, 397 (1906).
515. Dow Chemical Co., U. S. Patent 2413389 (1947).
516. Corning Glass Works, British Patent 583875 (1947).
517. —,   "   583878 (1947).
518. Dow Chemical Co., U. S. Patent 2405988 (1946).
519. Corning Glass Works, U. S. Patent 2413049 (1946).
520. —,   "   2413050 (1946).
521. Montclair Res. Corp. and Ellis-Foster Co., U. S. Patent 2413582 (1946).
522. H. Gilman and R. N. Clark, *J. Am. Chem. Soc.*, **69**, 1499 (1947).
523. Ethyl Corporation, *Chem. Eng. News*, **25**, 1888 (1947).
524. General Electric Co., U. S. Patent 2421653 (1947).
525. Corning Glass Works, British Patent 585400 (1947).
526. American Stove Co., U. S. Patent 2416531 (1947).
527. D. F. Wilcock, *J. Am. Chem. Soc.*, **69**, 477 (1947).
528. N. Bjerrum and E. Josefowicz, *Z. phys. Chem.*, **159**, 194 (1932).
529. C. A. Burkhard, E. G. Rochow, H. S. Booth and J. Hartt, *Chem. Rev.*, **41**, 97 (1947).
530. A. Stock, *Z. Elek.*, **32**, 341 (1926).
531. T. F. Anderson, *J. Chem. Physics*, **4**, 161 (1936).
532. K. A. Andrianov, *Org. Chem. Ind.*, *U.S.S.R.*, **6**, 203 (1939).
533. S. Shappiro, U. S. Patent 2356476 (1944).
534. J. G. Aston, R. M. Kennedy and G. H. Messerly, *J. Am. Chem. Soc.*, **62**, 2567 (1940).
535. J. G. Aston, *ibid.*, **63**, 2343 (1941).
536. E. B. Baker, A. J. Barry and M. J. Hunter, *Ind. Eng. Chem.*, **38**, 1117 (1946).
537. D. W. Scott, *J. Am. Chem. Soc.*, **68**, 2294 (1946).
538. N. V. de Bataafsche Pet. Maatschappi, French Patent 825079 (1938).
539. O. Behagel and H. Seibert, *Ber.*, **66**, 922 (1933).
540. Atlantic Refining Co., U. S. Patent 2160915 (1939).
541. North American Rayon Co., U. S. Patent 2030736 (1936).
542. —,   "   2030737 (1936).
543. —,   "   2030738 (1936).
544. W. L. Roth, *J. Am. Chem. Soc.*, **69**, 474 (1947).
545. A. Rosenheim, W. Loewenstein and L. Singer, *Ber.*, **36**, 1833 (1903).
546. S. Silver, *J. Chem. Physics*, **8**, 919 (1940).
547. G. Calingaert, H. A. Beatty and H. R. Neal, *J. Am. Chem. Soc.*, **61**, 2755 (1939).
548. R. M. Fuoss, *ibid.*, **65**, 2406 (1943).
549. D. H. Rank and E. R. Bordner, *J. Chem. Physics*, **3**, 248 (1935).
550. A. Bygden, *J. prakt. Chem.*, **96**, 86 (1917).
551. A. M. Patterson, L. T. Capell and M. A. Magill, *C.A.*, **39**, 5943 (1945).
552. B. N. Dolgov and Y. N. Vol'nov, *J. Gen. Chem.*, *U.S.S.R.*, **1**, 330 (1931).
553. H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, 1480 (1935).
554. C. Friedel and J. Crafts, *Compt. rend.*, **56**, 590 (1863).
555. —, —, *ibid.*, **61**, 792 (1865).
556. —, and A. Ladenburg, *ibid.*, **66**, 716 (1866).
557. Continental Oil Co., U. S. Patent 2129281 (1938).

559. C. Friedel and A. Ladenburg, *Ann. chim. phys.* (*5*), **19**, 390 (1880).
560. W. H. George, *Proc. Roy. Soc.*, **113A**, 585 (1927).
561. G. Giacomello, *Gazz. chim. ital.*, **68**, 422 (1938).
562. H. Gilman, A. H. Hanheim, G. O'Donnell and L. A. Woods, *J. Am. Chem. Soc.*, **67**, 922 (1945).
563. —, and C. C. Vernon, *ibid.*, **48**, 1063 (1926).
564. —, and L. A. Woods, *ibid.*, **65**, 435 (1943).
565. R. H. Smith and D. H. Andrews, *ibid.*, **53**, 3661 (1931).
566. G. Martin, *J. Chem. Soc.*, **103**, 119 (1913).
567. L. Malatesta and R. Pizzotti, *Gazz. chim. ital.*, **73**, 143 (1944).
568. —, —, *ibid.*, **72**, 491 (1942).
569. L. Glmakarova and A. N. Nesmeyanov, *J. Gen. Chem.*, *U.S.S.R.*, **9**, 771 (1929).
570. G. Jerusalem, *J. Chem. Soc.*, **97**, 2190 (1910).
571. R. H. Krieble and J. R. Elliott, *J. Am. Chem. Soc.*, **68**, 2291 (1946).
572. A. Ladenburg, *Ber.*, **4**, 726 (1871).
573. —, *Ber.*, **4**, 901 (1871).
574. —, *Ber.*, **5**, 319 (1872).
575. North American Rayon Co., U. S. Patent 2030739 (1936).
576. F. T. Wall and C. R. Eddy, *J. Chem. Phsyics.*, **6**, 107 (1938).
577. D. Vorländer, K. Kunze and E. Schroedter, *Ber.*, **58**, 1900 (1925).
578. D. B. Clapp, *J. Am. Chem. Soc.*, **61**, 523 (1939).
579. R. N. Lewis and A. E. Newkirk, *ibid.* **69**, 701 (1947).
580. G. S. Forbes and H. H. Anderson, *ibid.*, **69**, 1241 (1947).
581. F. C. Whitmore, L. H. Sommer, J. Gold and R. E. Van Strien, *ibid.*, **69**, 1551 (1947).
582. —, E. W. Puetrusza and L. H. Sommer, *J. Am. Chem. Soc.*, **69**, 2108 (1947).
583. H. A. Schuyten, J. W. Weaver and J. D. Reid, *ibid.*, **69**, 2110 (1947).
584. F. S. Kipping and R. Robison, *Proc. Chem. Soc.*, **29**, 374 (1913).
585. J. A. Meads and F. S. Kipping, *ibid.*, **30**, 6 (1914).
586. H. D. Cogan and C. A. Setterstrom, *Ind. Eng. Chem.*, **39**, 1364 (1947).
587. C. S. Miner, Jr., L. A. Bryan, R. P. Holysz, Jr., and G. W. Pedlow, Jr., *Ind. Eng. Chem.*, **39**, 1368 (1947).
588. C. M. Doede and A. Panabrossi, *Ind. Eng. Chem.*, **39**, 1372 (1947).
589. J. R. Patterson, Ind. Eng. Chem., **39**, 1376 (1947).
590. R. K. Iler and P. S. Pinkney, *Ind. Eng. Chem.*, **39**, 1379 (1947).
591. —, *Ind. Eng. Chem.*, **39**, 1384 (1947).
592. M. J. Hunter, M. S. Gordon, A. J. Barry, J. F. Hyde and R. D. Heidenreich, *Ind. Eng. Chem.*, **39**, 1389 (1947).
593. D. C. Atkins, C. M. Murphy and C. E. Saunders, *Ind. Eng. Chem.*, **39**, 1395 (1947).
594. H. W. Fox, P. W. Taylor and W. A. Zisman, *Ind. Eng. Chem.*, **39**, 1401 (1947).
595. G. M. Konkle, R. R. Selfridge and P. C. Servais, *Ind. Eng. Chem.*, **39**, 1410 (1947).
596. B. F. Goodrich Co., U. S. Patent 2399687 (1946).
597. C. P. Marsden, Jr.,   "   2329632 (1944).
598. Arthur D. Little, Inc., U. S. Patent 2335012 (1943).
599. Pittsburgh Plate Glass Co., U. S. Patent 2317891 (1943).
600. Corning Glass Works, U. S. Patent 2272342 (1942).
601. —, U. S. Patent 2215048 (1940).
602. Heaney Industrial Ceramics Co., U. S. Patent 2268589 (1942).
603. General Electric Co., U. S. Patent 2252500 (1941).

604. Carbide and Carbon Chemicals Corp., U. S. Patent 2253587 (1941).
605. —,   "   2046209 (1936).
606. —,   "   2027931 (1936).
607. —,   "   2027932 (1936).
608. Plaskon Co., U. S. Patent 2313678 (1943).
609. Radio Corp. of America, U. S. Patent 2314699 (1943).
610. E. I. du Pont de Nemours and Co., U. S. Patent 2404426 (1946).
611. I. D. Yudin, *Compt. rend. acad. sci., U.S.S.R.,* **25,** 614 (1939); *C.A.,* **34,** 4044 (1940).
612. The British Thomson-Houston Co., Ltd., British Patent 575667 (1946).
613. —,   "   575668 (1946).
614. —,   "   575669 (1946).
615. A. P. Laurie, U. S. Patent 1561988 (1925).
616. Austenal Laboratories, Inc., U. S. Patent 1909008 (1933).
617. Dow Chemical Co., U. S. Patent 2415389 (1947).
618. Owens-Corning Fiberglas Corp., U. S. Patent 2392805 (1946).
619. E. I. du Pont de Nemours and Co., U. S. Patent 2407181 (1946).
620. —,   "   2408654 (1946).
621. —,   "   2408655 (1946).   •
622. —,   "   2408656 (1946).
623. General Electric Co., U. S. Patent 2410737 (1946).
624. —,   "   2412470 (1946).
625. H. A. Gardner and E. Bielous, Am. Paint and Varnish Assoc., Circular 366, 327 (July, 1930).
626. —, and G. G. Sward, *ibid.,* Circular 421, 281 (October, 1932).
627. A. W. van Heuckenroth, *ibid.,* Circular 512, 228 (August, 1936).
628. H. A. Gardner and M. W. Westgate, *ibid.,* Circular 705, 412 (May, 1945).
629. E. Grimaux, *Compt. rend.,* **98,** 1434 (1884).
630. C. A. Burkhard and R. H. Kreible, *J. Am.Chem. Soc.,* **69,** 2687 (1947).
631. R. H. Krieble and C. A. Burkhard, *ibid.,* **69,** 2689 (1947).
632. A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *ibid.,* **69,** 2692 (1947).
633. L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *ibid.,* **69,** 188 (1947).
634. Elektroosmose, A. G., U. S. Patent 1132392 (1915).
635. E. I. du Pont de Nemours and Co., U. S. Patent 2392767 (1946).
636. National Benzol Association, U. S. Patent 1539342 (1925).
637. Newell L. Collins, U. S. Patent 1562940 (1925).
638. International Eng. Corp., U. S. Patent 2212992 (1940).
639. E. I. du Pont de Nemours and Co., U. S. Patent 2276314 (1942).
640. —,   "   2276315 (1942).
641. E. W. Abrahamson, I. Joffe and H. W. Post, *J. Org. Chem.,* **13,** 275 (1948).
642. M. E. Havill, I. Joffe and H. W. Post, *J. Org. Chem.,* **13,** 280 (1948).
643. A. Roxe, *Can. J. Res.,* **17**B, 385 (1939).
644. Corning Glass Works, British Patent 561226 (1944).
645. F. P. Price, *J. Am. Chem. Soc.,* **69,** 2600 (1947).
646. A. P. Kreshkov, *J. Gen. Chem., U.S.S.R.,* **17,** 81 (1947).
647. The British Thomson-Houston Co., Ltd., British Patent 590654 (1947).
648. J. E. Hackford, C. Shaw and W. E. Smith,   "   591149 (1947).
649. H. J. Emeleus and S. R. Robinson, *J. Chem. Soc.,* 1592 (1947).
650. L. H. Sommer, G. T. Kerr and F. C. Whitmore, *J. Am. Chem. Soc.,* 70, 434 (1948).
651. D. L. Bailey, L. H. Sommer and F. C. Whitmore, *ibid.,* **70,** 435 (1948).

652. L. H. Sommer, G. T. Kerr and F. C. Whitmore, *ibid.*, **70**, 445 (1948).
653. B. O. Pray, L. H. Sommer, G. M. Goldberg, G. T. Kerr, P. A. DiGiorgio and F. C. Whitmore, *ibid.*, **70**, 432 (1948).
654. E. W. Pietrusza, L. H. Sommer and F. C. Whitmore, *ibid.*, **70**, 484 (1948).
655. W. C. Schumb and A. J. Stevens, *ibid.*, **69**, 726 (1947).
656. N. Wright and M. J. Hunter, *ibid.*, **69**, 803 (1947).
657. C. W. Young, J. S. Koehler and D. S. McKinney, *ibid.*, **69**, 1410 (1947).
658. H. H. Anderson, *ibid.*, **69**, 3049 (1947).
659. G. S. Forbes and H. H. Anderson, *ibid.*, **69**, 3048 (1947).
660. F. C. Whitmore, L. H. Sommer and J. Gold, *ibid.*, **69**, 1976 (1947).
661. W. J. Jones, L. H. Thomas, E. H. Pritchard and S. T. Bowden, *J. Chem. Soc.*, 824 (1946).
662. General Electric Co., U. S. Patent 2426912 (1947).
663. Montclair Research Corp., U. S. Patent 2415017 (1947).
664. Continental Oil Co., U. S. Patent 2417833 (1947).
665. Remington Arms Co., U. S. Patent 2418935 (1947).
666. Imperial Chemical Industries, British Patent 583754 (1946).
667. Corning Glass Works, Canadian Patent 442271 (1947).
668. General Electric Co., U. S. Patent 2420912 (1947).
669. H. G. Emeleus and F. L. Sos, *Chem. and Ind.*, 450 (1946).
670. F. J. Jones, *Trans. Inst. Rubber Ind.*, **23**, 46 (1947).
671. M. J. Hunter, *Can. Chem. and Proc. Ind.*, **30**, (No. 2) 39 (1946).
672. C. E. Trautman, *Lub. Eng.*, **2** (No. 4), 143 (1946).
673. B. S. Prigozkin, *Legkaya Prom.*, (Nos. 9, 10) 29 (1946).
674. D. C. Young and M. Kin, *Plastics and Resins*, **5** (No. 12), 13 (1946).
675. Anonymous, *Fortune*, **35** (No. 5) 104 (1947).
676. S. L. Bass, *Chem. and Ind.*, 171 (1947).
677. G. de Senardens, *Assoc. suisse elec. Bull.*, **37**, 117 (1946).
678. R. Lulle, *La Nature*, 218 (1945).
679. R. B. Dow, *J. Colloid Sci.*, **2**, 81 (1947).
680. C. J. Bergendahl and C. E. Libby, *Paper Trade J.*, **125** (No. 10), 40 (1947).
681. F. Apelle, *Rev. gen. ele.*, **55**, 99 (1946).
682. Houston Paint and Varnish Prod. Club, Off. Digest Fed. Paint and Varnish Prod. Clubs, (No. 262) 534 (1946).
683. F. E. Halls, *Plastics (London)*, **10**, 376 (1946).
684. D. V. N. Hardy, *Endeavor*, **6**, 29 (1947).
685. J. A. McHard, *Chem. Eng.*, **54** (No. 2), 219.
686. S. McCready, *Can. Paint and Varnish Mag.*, **21**, (1946).
687. J. R. Patterson, Official Digest, Fed. Paint and Varnish Prod. Clubs (No. 266) 54 (1947).
688. S. K. Bishkin, *Paint, Oil, Chem. Rev.*, **109** (No. 23), 46 (1946).
689. L. Sanderson, *British Plastics*, **18**, 459 (1946).
690. Dow Corning Corp., "Dow Corning Silicones," 1947.
691. K. A. Andrianov, *J. Gen. Chem., U.S.S.R.*, **16**, 487 (1946).
692. B. Helferich and W. Reiman, *Chem. Ber.*, **80**, 163 (1947).
693. K. A. Andrianov, *J. Gen. Chem., U.S.S.R.*, **16**, 633 (1946).
694. —, *ibid.*, **16**, 639 (1946).
695. Y. N. Vol'nov, *ibid.*, **17**, 231 (1947).
696. K. D. Petrov, *ibid.*, **17**, 1099 (1947).

697. J. R. Gold, D. K. Bailey, L. H. Sommer and F. C. Whitmore, Unpublished.
698. B. A. Bluestein, Unpublished.
699. R. A. Benkisser and R. B. Currie, *J. Am. Chem. Soc.*, **70**, 1780 (1948).
700. K. D. Petrov and M. I. Itkina, *J. Gen. Chem.*, *U.S.S.R.*, **17**, 220 (1947).
701. Chem. Fabrik von Heyden, Belgian Patent 449077 (1943).
702. A. von Hoppel and L. G. Wesson, *Ind. Eng. Chem.*, **38**, 1121 (1946).
703. B. Stelnik, *Coll. Czech. Chem. Commun.*, **12**, 6 (1947).
704. M. M. Maglio, *Chem. Anal.*, **36**, 22 (1947).
705. L. M. White, *Anal. Chem.*, **19**, 432 (1947).
706. Dow Corning Corp., Private Communication, 1948.
707. J. T. Goodwin, Jr., W. E. Baldwin and R. R. McGregor, *J. Am. Chem. Soc.*, **69**, 2247 (1947).

Author Index

Numbers in parentheses refer to references

213

Subject Index

218